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LIQUEFACTION OF LOW RANK COALS

Phase 1

An Overview
Batch Hydrogenolysis of Lignite
Equilibrium Thermodynamics

A report for

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PREFACE

This document is the final report for a contract issued by Supply and Services Canada (DSS) on behalf of Energy, Mines and Resources Canada and covering the first of a multiphase study entitled "Potential for Liquefaction of Low-Rank Coals as a Future Source of Liquid Fuels". The contract number was OSQ77-00131 and the DSS file number 18SQ.23440-7-9059.

The work described in this report was conducted by a multi-disciplinary team of professionals from Beak Consultants Limited. The following personnel were co-investigators for this study and/or assisted in preparing this report.

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It is hoped that the results of this study and future work conducted during subsequent phases of this project will contribute to the development of resource conversion technology in Canada.

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Appreciation of certain individuals who have aided in the conception and completion of this work is sincerely expressed by the authors.

Thanks are due to Mr. G. Chapel of Manalta Coal for providing us, free of charge, samples of Saskatchewan lignite. The technical assistance provided by S. Hodd, B. McCormick, R. Fraser, P. Odom and M. J. Fenton from BEAK is gratefully acknowledged.

Finally, special thanks are due to Dr. J. Kelly, Scientific Advisor to this project from EMR. Dr. Kelly supplied us with EMR catalysts used for certain liquefaction experiments and provided continual co-operation, support, and technical guidance throughout the project.

SUMMARY

Objectives

The main objectives of this study were to review past work on low rank coal hydrogenolysis, to statistically quantity the effect of varying operating conditions on product quantity and quality obtained from batch liquefaction of a lignite, and to develop a thermodynamic model of non-ideal three-phase reacting systems such as liquefaction.

Overview

A literature survey on this subject showed that present day developments in coal liquefaction originated from the early Bergius and Fisher-Tropsch processes. Poor quality products were obtained from these processes due to rapid catalyst deactivation by the sulphur present in coal. Eventually, the processes were improved by employing methanol synthesis catalysts consisting of oxides and sulphides of molybdenum, tungsten and group VIII metals. All of the early commercial processes emphasized the synthesis of gasoline, diesel fuel and paraffin wax.

Attempts were made to obtain guidelines relating liquid yields and conversions from coal liquefaction with reactive maceral content, coal rank and elemental composition of the feed. In general, conversion was positively correlated with per cent reactive macerals in the feed. The highest liquid oil yields were obtained from high volatile bituminous coal, which contains relatively high hydrogen (5 to 6%) and low oxygen (8 to 9%) contents on a moisture and ash free (maf) basis. Other factors, such as composition of the mineral matter and coal pre-treatment conditions, affected conversions, especially for low rank coal.

The solvent used for liquefaction had a determining effect on conversion and quality of the liquid products. Solvents having hydrogen donor and transfer properties were essential in directing hydrogenolysis to liquid products rather than gases and solids. Other solvent properties such as solubility parameter, boiling point and dielectric constant affected the reaction.

The principal catalysts used for primary conversion were oxides of cobalt, molybdenum and nickel; the catalysts used for hydrogenation of the liquid oils obtained from liquefaction were tungsten and nickel sulphides. However, the ash present in lignites was sufficient to catalyze their conversion and added catalysts did not increase product quantities from their hydrogenolysis.

A number of liquefaction processes have been developed to produce synthetic crude, naphtha and synthesis gas. However, none have been tested on a commercial basis.

Equilibrium Thermodynamics

Numerous methods have been developed to calculate phase data for non-ideal vapour-liquid equilibria. Therefore, the extension of these methods was used in this project for modelling simultaneous vapour-liquid and chemical equilibria of coal liquefaction.

The approach taken was to derive an expression for the free energy of a multi-component system as a function of the chemical compositions of all phases present. The expression involved mixture fugacity coefficients which were estimated with a Redlich-Kwong equation of state. The equilibrium product distribution of coal liquefaction could then be calculated by determining the component mole numbers at the minimum of the free energy function for a given temperature and pressure. The numerical method employed was the Sequential Unconstrained Minimization Technique (SUMT).

At operating conditions used for coal liquefaction, the model predicted principally a liquid phase. This created a seemingly non-equilibrium situation which caused the computations to diverge. Therefore, no results were yet available pertaining to the effect of operating conditions on equilibrium composition.

The fact that a liquid oil phase was predicted to predominate is an encouraging result of our preliminary investigations. As well, solving the problem of divergent calculations was close at hand. Therefore, continuation of work on liquefaction thermodynamics was recommended. Modification of the existing computer programme and improvement of the thermodynamic data base would be required. The development of this method would allow prediction of the quantity of gas dissolved in and the phase structure of a reacting mixture as well as aid engineering design and kinetic modelling of coal liquefaction.

Batch Hydrogenolysis of Lignite

During this study, batch liquefaction of a Saskatchewan lignite was conducted. The results of the first set of experiments, without added catalysts, were fitted to a statistical model using a partially replicated 2^4 factorial design. A second set involved eight catalytic deoxygenation and hydrogenation experiments using cobalt-molybdate, nickel and iron catalysts.

Each experiment consisted in mixing known quantities of pulverized raw lignite with anthracene oil at a solvent/feed mass ratio of 2.8/1, and reacting the mixture with carbon monoxide and hydrogen. The range of experimental variables studied were 653 K to 733 K reaction temperature, 7.1 MPa to 11.1 MPa initial pressure, 10 minutes to 50 minutes residence time at reaction temperature, and initial carbon monoxide mole fraction of 0.25 to 0.75.

The highest conversions and liquid oil yields obtained experimentally were 85.3 per cent and 63.4 per cent, respectively on a maf basis. Therefore, sufficient product quantity could be obtained in a commercial liquefaction process.

The results showed that increasing temperature increased conversion. An increase in pressure also increased conversions except when a low residence time and initial carbon monoxide content were used. This latter condition favoured coking.

For short residence times (10 to 40 min, depending on initial carbon monoxide content), higher temperatures produced greater yields but for longer residence times, lower temperatures increased oil yields. Optimum liquid yields were obtained using a low temperature (< 653 K), high carbon monoxide concentration in the reactant gas, high pressures (> 11 MPa) and long residence times (> 50 min).

The initial feed (lignite plus anthracene oil) contained 5.4 per cent hydrogen, 7.9 per cent oxygen, 0.9 per cent nitrogen and 0.5 per cent sulphur (maf basis). The liquid oil products had a hydrogen content increased to 5.7 - 6.4 per cent and oxygen decreased to 2.0 - 3.6 per cent. The nitrogen and sulphur contents were not significantly reduced, which was probably due to the already low concentration of these elements in the feed. In general, greater hydrogenation but less deoxygenation occurred at lower reaction temperatures.

The actual oxygen content of the liquid products may be lower than reported. During product recovery, the liquids were filtered in air at 380 K which probably resulted in oxidation of the products. Therefore, this oil may have a low enough oxygen content (< 1.5%) to be used as a boiler fuel or synthetic crude for upgrading.

The main components of the gas phase were hydrogen, carbon dioxide and methane. After scrubbing to remove carbon dioxide, this gas would be highly suitable as a synthesis gas used for petrochemical feedstock, industrial fuel gas or recycle gas for liquefaction. No distinct pattern was observed for the evolution of the carbon monoxide/hydrogen ratio.

Addition of one of the four catalysts for primary liquefaction of raw lignite did not appear to increase conversions or total liquid oil yields, but increased the light oil fraction. Catalytic treatment of the product oil did not seem to add hydrogen but decreased oxygen content. However, adsorption of oxygen from air into the oils masked the deoxygenation reaction.

During the second phase of this project, the liquefaction apparatus will be modified to solve problems encountered with air contacting the oils and a varying carbon monoxide/hydrogen ratio. The more precise results thus obtained will show the true deoxygenation capacity of the catalysts and allow greater control of the reaction.

As well, further catalytic screening experiments will be conducted. Using externally added catalysts during liquefaction can improve product quality by increasing the hydrogen/carbon ratio and decreasing the oxygen, sulphur and nitrogen content of the liquid oils. As well, the severity of operating conditions can be lowered while maintaining product quantity and quality.

The results of this study confirm that lignite liquefaction is a technically feasible process. Sufficient product quantity can be obtained. As well, recoverable catalysts may improve product characteristics and decrease the severity of operating conditions. Work conducted during subsequent phases this project should demonstrate these observations.

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INTRODUCTION

Background

On 2 December 1977, Beak Consultants Limited (BEAK) were awarded a contract by Supply and Services Canada (DSS) on behalf of Energy, Mines and Resources Canada (EMR), to conduct a study on the potential of domestic low-rank coals as a source of synthetic fuels in Canada. The contract covered the first of a multiphase project.

This report describes the work conducted during Phase 1 and the findings obtained.

Objectives

The objectives of the first phase included the following:

1. Review of past work on low rank coal hydrogenolysis.
2. Characterization of products obtained from liquid phase hydrogenolysis of lignites.
3. Determination of the effect of varying operating conditions on product quantity and quality obtained from batch lignite liquefaction.
4. Determination of optimum reactor conditions for the production of liquid oils from lignite.
5. Thermodynamic modelling of a non-ideal three-phase reacting system such as hydrogenolysis.

Definition of Terms

The terminology used to describe fuel conversion processes has generally been poorly defined. This section will attempt to correct the situation by defining commonly utilized terms, especially in the context intended for this report.

Conversion is the transformation of a carbon-containing substance into gaseous, liquid or solid compounds having improved fuel characteristics or higher carbon content than the original material. The thermal efficiency of a conversion process is defined as the heating value of all products divided by the heating value of the feed.

Figure 1 presents alternate routes for the conversion of organic materials to combustible fuels. Three main reactions may be used: pyrolysis, gasification and hydrogenation.

Pyrolysis is the thermal decomposition of complex molecules into simpler units. The pyrolysis of solid fuels produces three major product streams:

(a) a gas composed mainly of hydrogen (H_2), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2) and steam;

(b) liquid tars;

(c) a solid char composed of coke and ash.

This type of reaction is endothermic (absorbs heat) and occurs in the absence of air or oxygen.

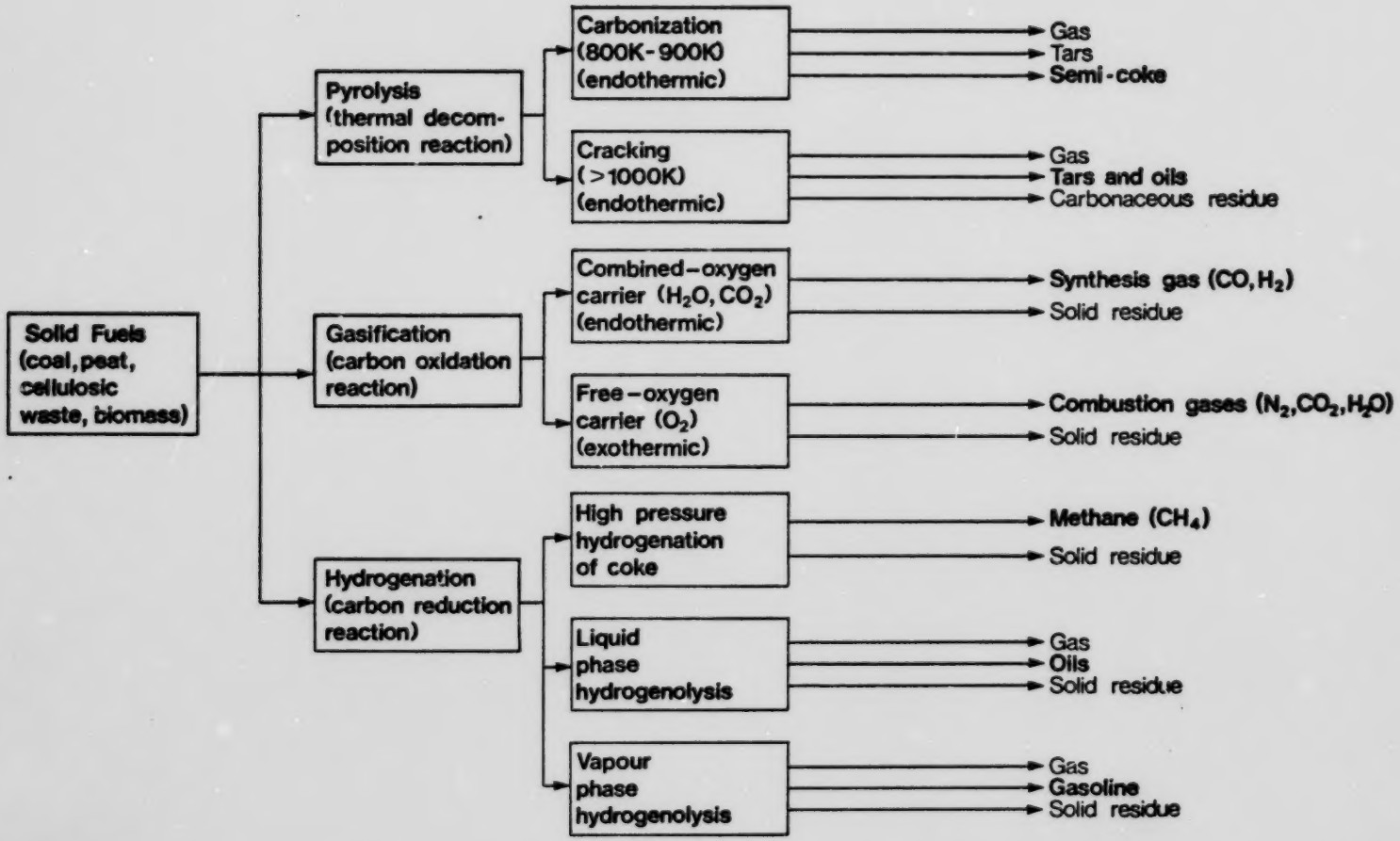
Pyrolysis may be subdivided into carbonization or cracking. Carbonization is the conversion of a carbon-containing substance to a solid residue containing a higher percentage of carbon than the original material. Cracking is a process used to reduce the molecular weight of organic compounds by thermally breaking molecular bonds, producing mainly gas and liquid hydrocarbons. Carbonization generally occurs at lower temperatures (< 1000K) than cracking.

Gasification is the oxidative conversion of carbon compounds to a gas. The oxidizing agent may be free oxygen in which case the reaction is an exothermic combustion, producing carbon dioxide and an inorganic residue. If the feed is oxidized by a combined-oxygen carrier, such as steam, the reaction is endothermic and produces mainly a synthesis gas.

Hydrogenation is the chemical reduction of organic compounds with hydrogen to produce liquid or gaseous hydrocarbons. High pressure hydrogenation of coke is used for methane synthesis. A destructive hydrogenation (hydrogenolysis) in liquid phase is used to produce intermediate oils with a boiling point between 450 K and 600 K; vapour phase hydrogenolysis can catalytically convert middle oil vapours into gasoline. Liquid phase hydrogenolysis has been commonly called "liquefaction"; in this report, both hydrogenolysis and liquefaction will be used synonymously to signify a conversion process involving principally liquid phase hydrogenolysis.

Figure 1

Alternate Routes for the Conversion of Solid Fuels



Scope of Work

Phase 1 of this project was divided into three tasks:

1. A literature review of published studies on liquefaction of low rank coals and discussion of findings. Chapter 1 provides the results of this task.

2. Batch liquefaction of lignite was conducted. One set of experiments, without added catalysts, were modelled using a partially replicated 2^4 factorial design. A second set involved eight catalytic deoxygenation and hydrogenation experiments using cobalt-molybdate, nickel and iron catalysts. Procedures are described and a discussion of results is given in Chapter 2.

3. A thermodynamic model for high pressure non-ideal reactions such as liquefaction was developed. The model involved expressing the total free energy of the reacting system as a function of only the molar concentrations of the components present at equilibrium. The equilibrium product distribution was predicted by determining the values of the component mole numbers which minimized the free energy at a specified temperature and pressure. The method used and results are presented in Chapter 3.

The scope of work proposed for Phase 2 of this project was determined in conjunction with the Scientific Authority from EMR and was based on results presented in this report. A summary of Phase 2 work is included as Appendix 1.

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CHAPTER 1

OVERVIEW OF LOW-RANK COAL HYDROGENOLYSIS

1.0 ORIGIN AND CONSTITUENTS OF COAL

Coals were formed from decaying plant material in two-distinct phases (Parks, 1963): the biochemical or peat formation phase and the dynamo-chemical or coalification phase.

During the first phase, peat was formed from the biochemical degradation of plant remains (phyterals) under wet anaerobic conditions. Two major factors influencing the rate of plant degradation were chemical stability of various plant components, and swamp water flow configuration and chemical nature.

Peat constituents may be classified into the following categories:

peptides and starches
celluloses and hemicelluloses
lignins
humic substances
waxes and resins
inorganic salts

Microorganisms readily decompose proteins and starches but to a lesser extent, the celluloses. Lignin is more resistant to decay but does undergo a progressive change to humic substances in a process called humification. Humic substances are broadly divided into three types of materials (Schnitzer and Khan, 1972): fulvic acids, humic acids and humins. Of these, humic acids and particularly humins are highly resistant to chemical transformation and thus are often found in coals. Waxes and resins are not normally degraded by microorganisms.

During periods of geological change, peat deposits were covered by sedimentary rocks and subjected to high temperatures and pressures. This resulted in a metamorphic transformation of peat into coal which is considered the dynamo-chemical or coal formation (coalification) phase. This phase is subdivided into three stages (Schopf, 1948) which reflect a progressive alteration of phyterals: lignitic, bituminous, and anthracite stages. Coal constituents of organic origin (macerals) are identified in Tables 1 and 2. Lignites and other coals have two maceral groups common to each other, exinite (or liptinite) and inertinite. Huminite in lignites originates from humic substances found in peat while vitrinite in higher ranking coals is formed from transformed cellulosic materials.

Table 1: Classification and source of lignite macerals[1]

Maceral group	Maceral	Source
Huminite	Textinite	Ungelified cell-wall material
	Ulminite	Gelified plant tissues with recognizable cell structure
	Attrinite	Humic detritus
	Densinite	
	Gelinite	Formless humic gels
	Corpohuminite	Secondary colloidal cell excretions, and primary cell infillings (tannins)
Liptinite	Sporinite	Spore exines
	Cutinite	Cuticles
	Resinite	Resins
	Suberinite	Cork tissues
	Alginite	Algae
	Liptodetrinite	Fine particles of liptinite
Inertinite	Fusinite	As in hard coals (Table 2)
	Semifusinite	
	Macrinite	
	Sclerotinite	
	Inertodetrinite	Fine particles of inertinite

[1] from Davis et al. (1976)

Table 2: Classification and source of coal macerals[1]

Maceral group	Maceral	Source
Vitrinite	Telinite (cell walls)	Woody tissues, bark, leaves
	Collinite (cell fillings, structureless vitrinite)	
Exinite (or liptinite)	Resinite	Resins
	Sporinite	Spore exines
	Cutinite	Cuticles
	Alginite	Algae
Inertinite	Micrinite (massive and granular)	Plant materials
	Fusinite	Woody tissues
	Semifusinite	Woody tissues
	Sclerotinite	Fungal sclerotia, hyphae

[1] from Davis et al. (1976)

2.0 HISTORICAL REVIEW OF EARLY COAL HYDROGENATION STUDIES

2.1 Initial Developments to 1945

Excellent accounts of the early developments of coal conversion by liquid phase hydrogenolysis and hydrogenation can be found in publications by Storch (1963) and Donath (1963). Their reviews covered both the work before the development of commercial plants in Germany and England, and the later research and development work in the United States, Japan, France and Canada in the early fifties. The following sections present a summary of this early work.

2.1.1 Research on Solvent Extraction of Coal

The first accounts of coal conversion were given by Berthelot (1869, 1870) and involved the extraction of oil from coal using hydriodic acid at temperatures up to 400 K. Some depolymerization occurred which resulted in a 60% oil yield and a 30% yield of bitumen-like residue. Coals of various ranks as well as wood (dry and partially carbonized) produced similar yields.

In 1912, a high pressure technique was developed for ammonia synthesis which led to the application of high pressure hydrogenation to solvent extraction of coal (Fisher and Tropsch, 1918) using phosphorus as a catalyst. Fisher (1925) later employed sodium formate as a catalyst and demonstrated that, within certain limits, the yield of liquid products increased with decreasing coal rank. In these early German processes the use of a vehicle or pasting oil to slurry the coal may have acted as an extractive medium for the feed.

Continued development of the solvent extraction process produced considerable data on the subject, mainly through the efforts of Pott and Broche (1927, 1934) who originated numerous patents and correlations between optimum extraction temperature, solvent mixtures and various coal ranks. The initial patent registered in Britain in 1927 indicated that a 2/1/2 mixture of tetrahydronaphthalene (tetraline)/phenol/naphthalene proved optimum for coal extraction. A tar-like substance was obtained from lignites and brown, bituminous and sub-bituminous coals at temperatures ranging from 470 to 480 K. These patents and relationships were reviewed by Storch (1963).

The modern supercritical extraction of coal (Maddocks and Gibson, 1977) developed by the National Coal Board of England is a direct extension of early solvent extraction work.

2.1.2 High Pressure Hydrogenation

In 1912, Bergius developed a process, which now bears his name (Bergius, 1912; Bergius and Billwiller, 1914), by applying high pressure technology to hydrogenation. Coal and carbonaceous materials were initially hydrogenated at 10 MPa and 420 to 530 K. Heavy recycle oil was used as pasting oil and a very cheap disposable compound (luxmasse) containing iron and titanium was added as a catalyst. A 1 Mg/day pilot plant was developed by 1922.

Bergius' process using mainly brown coals, resulted in poor quality products, probably due to prolonged contact times (2 hours) and very poor hydrocracking and hydrorefining properties of the catalytic mixture. Polymerization or condensation of primary products following coal dissociation led to products with high oxygen, nitrogen and sulphur contents.

By the early twenties it was evident that the Bergius Process would require better catalysts if high quality fuel products were to be obtained. Attempts to employ active catalysts were hindered by the presence of sulphur in coal which tends to deactivate hydrogenation catalysts.

Eventually, Pier (1953) discovered that a few of the oxide catalysts used in methanol synthesis since 1923 were both highly active and sulphur resistant (Donath and Hoering, 1977). The sulphides and oxides of molybdenum, tungsten and group VIII metals were subsequently used to catalyze four main hydrogenolysis and hydrogenation reactions: cleavage of coal macromolecules, hydrogen addition, carbon-carbon bond splitting and elimination of heteroelements (sulphur, oxygen and nitrogen).

Pier's group improved phase contact by sub-dividing the process into two stages:

a. hydrogenolysis of a coal-recycle oil mixture using finely dispersed catalysts producing an oil of medium boiling point;

b. vapour phase hydrocracking of the "middle oil" using fixed bed catalysts.

A summary description of German coal and tar hydrogenation plants is given in Table 3.

In 1935, a coal hydrogenation plant was constructed at Billingham, England which initially treated bituminous coals but later used coal tar (Gordon, 1935; 1956).

Further experimentation on coal hydrogenation was conducted in England (Booth et al, 1937; 1938), Japan (Leopold, 1937; Shibata, 1953), France (Audibert, 1936; Vallette, 1937), Italy (Fauser, 1937; Kaftal, 1942), Canada (Warren and Bowles, 1940) and the United States (Storch, 1963; Donath, 1963; Storch et al., 1941). This resulted in the construction of only one full-scale plant, in Italy, which was designed mainly for the hydrogenation of heavy petroleum residues.

In the 1930's, a series of articles on coal hydrogenation were published to foster international cooperation in this field (Gordon, 1931, 1933, 1935; Gordon and Pier, 1935; King, 1938).

2.1.3 Hydrogenolysis with Carbon Monoxide

Present day developments in coal hydrogenolysis using carbon monoxide and carbon monoxide/hydrogen mixtures originated from early German research reported in 1921. Brown coals were reacted in the presence of carbon monoxide and water producing a tarry substance (Fisher and Schrader, 1921). This discovery was largely ignored until the late 1960's when the U.S. Bureau of Mines undertook extensive research in this field.

2.2 Post-war Developments

2.2.1 Commercial Operations

After 1945, only three German plants continued to operate and, of these, only the Leuna works treated substantial amounts of brown coal. A new plant was constructed in Siberia out of dismantled German material and produced 1 Tg per year of aviation gasoline from coal. The Brüx plant in Czechoslovakia operated on brown coal tar. The Billingham plant gradually shifted from a bituminous coal/creosote mixture to creosote oil before shutting down in 1958. All of these commercial plants emphasized the synthesis of gasoline, diesel fuel and paraffin wax.

Table 3: German coal and tar hydrogenation plants[1]

Start-up Date	Location	Feedstock	Capacity Mg/year	Present Status
1927	Leuna, W. Germany	Brown coal, brown coal tar	650,000	in operation
1936	Böhlen, W. Germany	Brown coal tar	250,000	in operation
1936	Magdeburg, W. Germany	Brown coal tar	250,000	dismantled
1936	Scholven, E. Germany	Bituminous coal	250,000	coke-oven light oil refining and crude oil hydrogenation
1937	Welheim, E. Germany	Pitch	130,000	no hydrogenation
1939	Gelsenberg, E. Germany	Bituminous coal	400,000	crude-oil hydrogenation
1939	Zeitz, W. Germany	Brown coal tar	280,000	in operation
1940	Lützkendorf, W. Germany	Tar, oil	50,000	no hydrogenation
1940	Pölitz, Poland	Bituminous coal, oil	700,000	dismantled
1941	Wesseling, E. Germany	Brown coal	250,000	crude-oil hydrogenation
1942	Brüx (Most), Czechoslovakia	Brown coal tar	600,000	in operation
1943	Blechhammer, Poland	Bituminous coal, tar	420,000	dismantled

[1] from Hoering and Donath (1958)

2.2.2 U.S. Developments

Bench-scale hydrogenation of U.S. lignites and bituminous coals was conducted by the U.S. Bureau of Mines (Wiley and Anderson, 1950; 1951; 1952) to produce design criteria for a pilot plant. The work resulted in the construction of a 50 Mg per day plant in Louisiana which operated from 1949 to 1953 to produce synthetic fuels. Discovery of oil fields in the middle east rendered such operations economically unfeasible.

Some pilot-scale work continued, resulting in the development of the hydrocarbonization process using high temperatures and low pressures (Clark et al., 1950).

Major efforts in this field resumed in the late 1950's through the 1970's. The results of this work are described in subsequent sections.

3.0 EFFECT OF FEED COMPOSITION ON COAL HYDROGENOLYSIS

3.1 General Considerations

Attempts have been made to obtain guidelines relating liquid yields from coal hydrogenolysis with reactive maceral content, coal rank and carbon or hydrogen present in the feed. Reviews on this subject have been published by Davis et al. (1976), Donath (1963), Fisher et al. (1942) and Montgomery (1974). Although generalizations of past work are difficult to make due to different experimental conditions used by various workers, broad interpretations are possible.

3.2 Effect of Carbon and Hydrogen Content

Table 4 presents elementary compositions of peat as a function of their degree of humification. The hydrogen content is fairly constant but as humification increases, oxygen content decreases and carbon content increases.

Few studies have considered in depth the hydrogenolysis of peat. However, recent work at the University of Sherbrooke has indicated that highly humified peat produces greater oil yields than less humified peat (Cavalier and Chornet, 1977).

The hydrogen, carbon and oxygen contents of various coals are presented in Figure 1, (Meunier, 1958). This diagram shows that the hydrogen content of lignite, sub-bituminous and bituminous coals is approximately constant and is the highest found in coals. Therefore, these types of coal have the potential of producing the highest liquid yields during a conversion reaction.

Figure 2 summarizes the results of early German work on hydrogenolysis of lignite and sub-bituminous coals, using a continuous flow pilot plant operating at 62 MPa, process temperatures between 675 K and 760 K, and iron catalysts. The curves in Figures 2c and 2d represent various coals containing a particular amount of hydrogen attached to 100 g of carbon. This parameter, called the net hydrogen content of coal, does not include hydrogen attached to sulphur, oxygen or nitrogen molecules. For a given per cent carbon in coal, the higher net hydrogen contents, which are found in lignites, tend to lower gas yield and asphaltenes in the product mixture but increase oil space time yield. Therefore, oil produced from lignite should be easier to separate from the heavy letdown product than that produced from other coals (Donath, 1963).

Table 4: Elementary composition[1] of peats

Degree of Humification	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur
Low	48-53	5.0-6.1	40-46	0.5-1.0	0.1-0.2
Medium	54-58	5.5-6.1	34-38	0.8-1.1	0.1-0.3
High	59-63	5.1-6.1	31-34	0.9-1.9	0.2-0.5

[1] per cent by weight moisture and ash free peat

Figure 1

Carbon, Oxygen and Hydrogen Content of Coals (from Meunier, 1958)

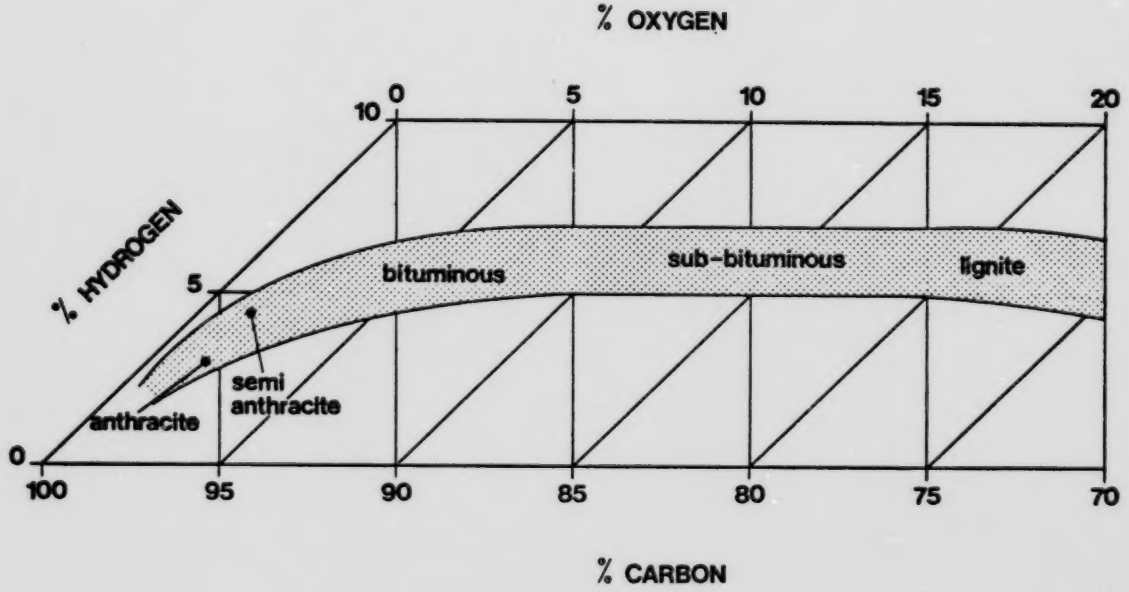
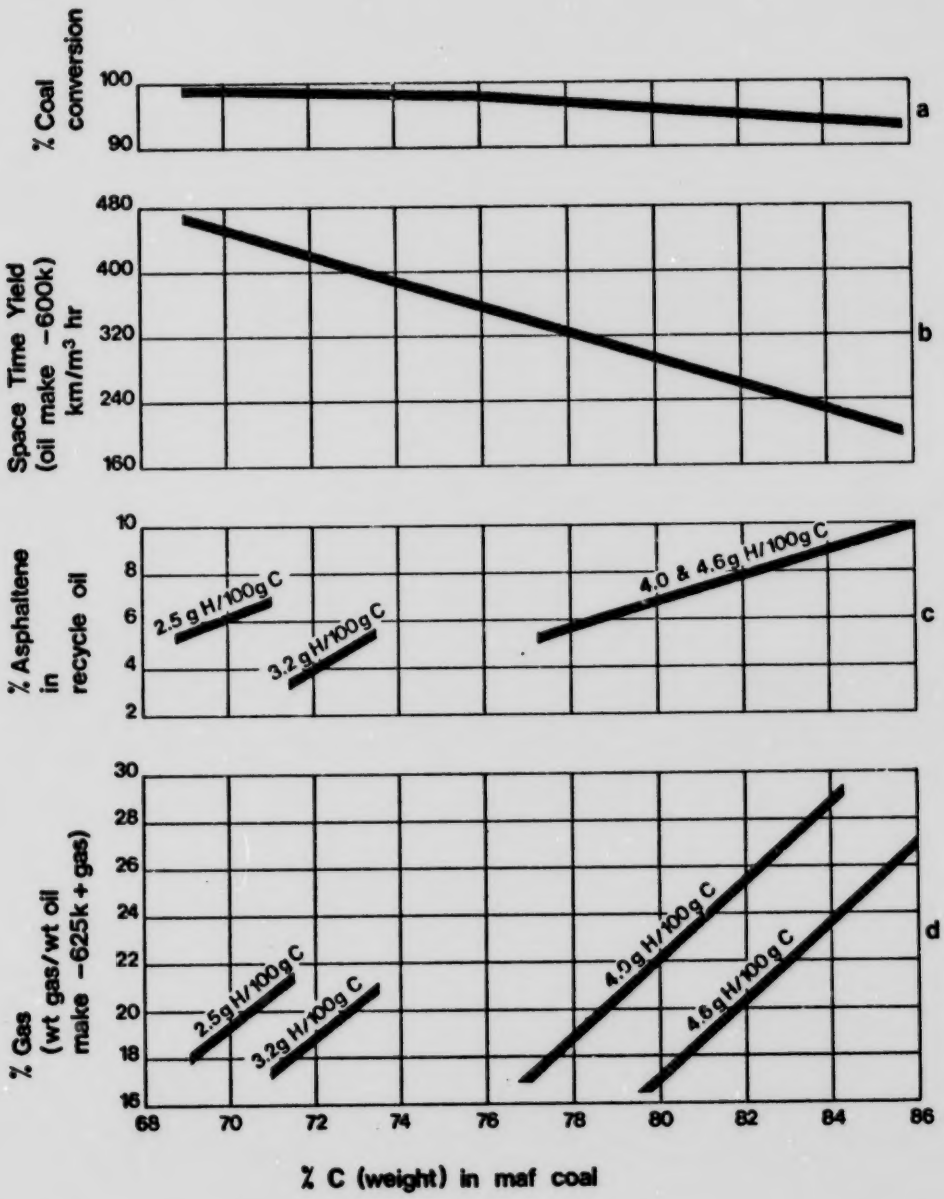


Figure 2

Effect of Hydrogen and Carbon Content on Coal Hydrogenolysis (from Donath, 1963)



The results from the hydrogenolysis of bituminous coals did not produce correlations similar to those found in Figure 2.

3.3 Effect of Coal Rank

Early Canadian work (Warren et al., 1939) involved batch and continuous flow hydrogenolysis of various coals. Table 5 summarizes their findings obtained from continuous flow hydrogenolysis at 20 MPa, process temperature of 720 K and tin (II) oxide (SnO) as catalyst. The results show that high volatile bituminous coals produce higher liquid yields than other coals, which seems to conflict with observations presented in the previous section. This anomaly may be explained considering that different operating conditions are used by various research groups.

The Canadian workers also reported an apparent relation between nitrogen content in coal and liquid yield. Despite its potential significance, no other evidence of this correlation has been published to date.

Early work at the U.S. Bureau of Mines (Fisher et al., 1942) focussed on correlations between structural aspects of coal constituents and liquid yields. Their studies showed that coal components which are translucent in thin sections under a microscope were readily converted to liquids, whereas opaque constituents were resistant to hydrogenolysis (Storch, 1963). Furthermore, spores, resins, oil algae and wood debris yielded mainly aliphatic hydrocarbons whereas anthraxyllon (vitreous-appearing component of coal derived from woody tissues) converted to aromatic hydrocarbons. Liquid yields obtained from bright coals (containing more than 5% anthraxyllon and less than 20% opaque matter) could be correlated with carbon content but no such relation could be obtained from the hydrogenolysis of cannel (highly volatile bituminous) coal or splint (hard bituminous) coal.

A summary of experimental results obtained at the U.S. Bureau of Mines is presented in Table 6. The highest oil yields were obtained from high volatile bituminous coal. Low-ranking coals (lignite and sub-bituminous) were highly sensitive to experimental conditions (Fisher et al., 1942): in general, higher pressures and reaction times caused an increase in oil yield but temperature had a variable effect. However, differences in petrographic composition may have obscured the effect of coal rank.

Table 5: Product yields[1] from coal hydrogenolysis at the Canadian Department of Mines[2]

Location	Rank	Liquid oil[2] Yield %	Liquid oil[3] Yield L/kg
Crowsnest, B.C.	medium volatile	62.0	0.621
Vancouver Island, B.C.	high volatile A	66.8	0.671
Durham, England	high volatile A	71.5	0.716
Sydney, N.S.	high volatile A	77.2	0.771
Nicola, B.C.	high volatile B	73.8	0.741
Saunders, Alta.	high volatile C	53.3	0.536
Drumheller, Alta.	sub-bituminous B	62.5	0.626
Edmonton, Alta.	sub-bituminous C	57.7	0.576
Bienfait, Sask.	lignite	56.6	0.567

[1] moisture and ash free coal basis

[2] from Warren et al. (1939)

[3] fraction distilled at less than 575 K

Table 6: Product yields[1] from coal hydrogenolysis at the U.S. Bureau of Mines[2]

Location	Rank	Liquid Oil Yield %
Jefferson Co., Alabama	high volatile A	60.0
Allegheny Co., Pennsylvania	high volatile A	70.5
Franklin Co., Illinois	high volatile B	70.5
King Co., Washington	high volatile C	68.5
Weld Co., Colorado	sub-bituminous B	63.0
Rosebud Co., Montana	sub-bituminous B	60.0
Sheridan Co., Wyoming	sub-bituminous B	68.5
Mercer Co., North Dakota	lignite	54.5
Ward Co., North Dakota	lignite	52.0

[1] weight per cent of moisture and ash free coal

[2] from Storch (1963)

3.4 Effect of Petrographic Composition

Batch autoclave tests conducted at 660 K, 24 MPa and reaction time of one hour have shown that conversion of sub-bituminous and higher ranking coals is positively correlated with vitrinite content (Davis et al., 1976). The correlation for sub-bituminous coal is shown in Figure 3.

In general, the per cent coal conversion from hydrogenolysis was found to be positively correlated with per cent reactive macerals in various coals (see Figure 4). Reactive macerals are considered to be vitrinite plus exinite for high ranking coal, and huminite plus liptinite for lignites. Inertinite is generally resistant to hydrogenolysis.

For high vitrinite coals, the viscosity of the product oil tended to be positively correlated with coal rank (Given et al., 1975). However, no relationship was observed between per cent asphaltenes in the product and coal rank.

Optimum conversions of high ranking and highly volatile materials were obtained for coals having 70 to 100% (volume % maf) total reactive macerals and having 0.49 to 1.02% reflectivity in oil.

The dependence of conversion on reactive macerals is less evident for lower ranking coals. Both coal pre-treatment conditions and the composition of mineral constituents seem to affect conversions of low rank coals more than high ranking coals.

The catalytic effect of minerals present in coal ash is not clearly understood. For example, when sodium, which is a constituent of coal ash and normally catalyzes hydrogenolysis reactions, was added to lignites, their conversion and product oil yield were not appreciably increased. However, adding sodium seemed to produce an oil of lower viscosity (Given et al., 1975). Future work in the area should concentrate on studying types of active catalytic sites in the reaction mixture and reaction mechanisms. Metal constituents should be identified as well as their chemical configuration that is inorganic salt, organic complex or chelate. Particular reactions susceptible to catalysis from coal ash constituents should be identified. These may include stabilization of fluid pitches from macerals or humic substances, hydrogenolysis of the pitches, and nucleation of mesophases from pitches leading to semi-coke rather than liquid products. As well, the effect of other elements, such as sulphur and nitrogen, should be determined.

Figure 3
Dependence of Conversion of a Sub-bituminous Coal on Vitrinite Content (from Davis et al., 1976)

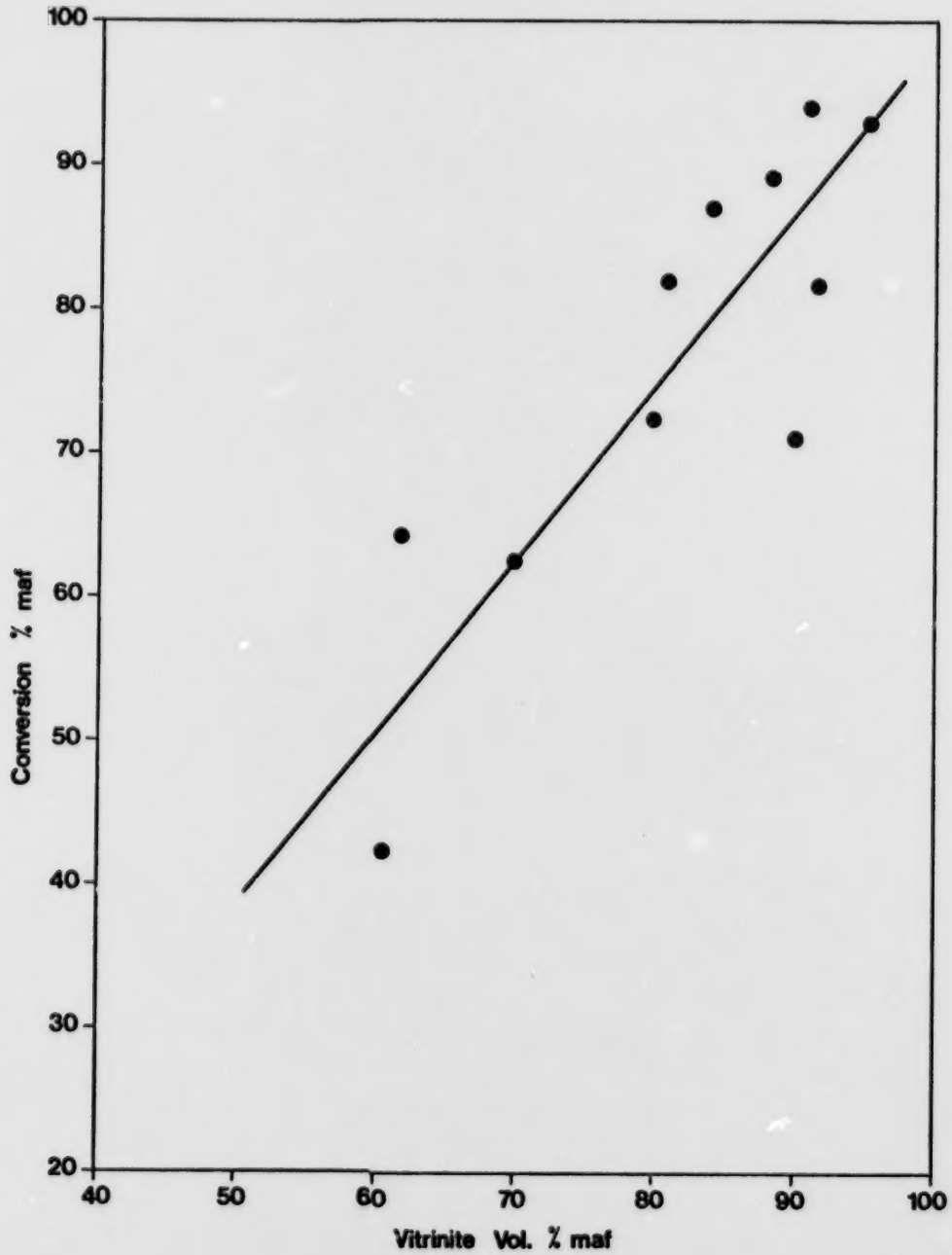
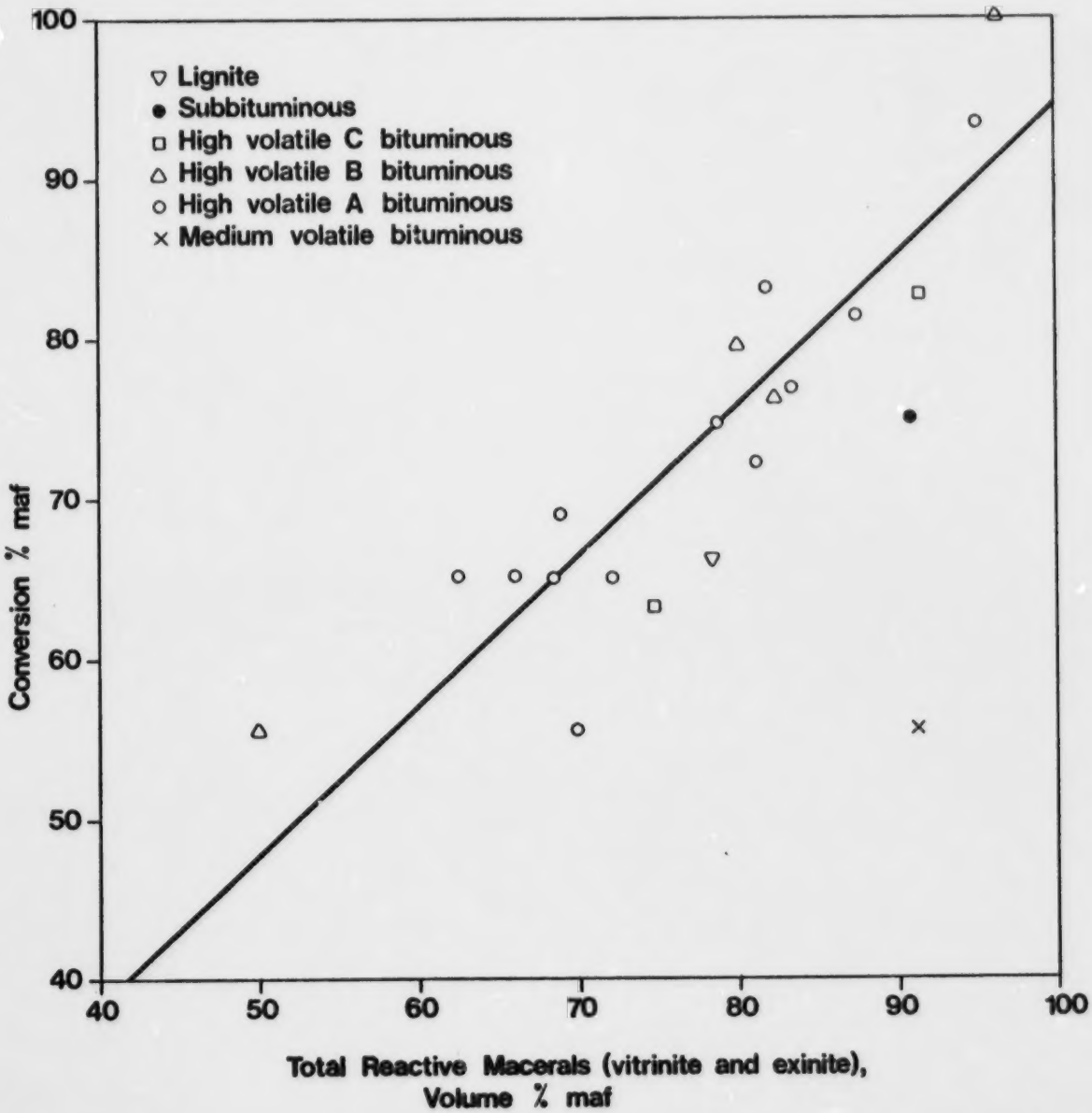


Figure 4

Dependence of Conversion on Reactive Maceral Content (from Given et al., 1975)



4.0 CHEMICAL ASPECTS OF COAL HYDROGENOLYSIS

4.1 Liquefaction of Oxygenated Coals

To produce a commercially acceptable product from liquefaction of oxygenated coals, substantial amounts of oxygen must be removed. Since this probably could not be accomplished during primary conversion, product upgrading must be conducted either in-situ or during secondary reactions. This is not necessary when reacting high ranking bituminous coals since they contain approximately one third of the oxygen found in lignites.

Both carbon monoxide and water play an important role during hydrogenolysis of oxygenated coals but neither affects conversion of higher rank coals.

Carbon monoxide seems to promote hydrogenolysis of oxygenated materials in three ways (Fisher and Schrader, 1921; Appell, 1976; Appell and Wender, 1968; Appell et al., 1969; 1969; 1972; 1975). Firstly, carbon monoxide acts as an oxygen scavenger to produce carbon dioxide. This reaction is kinetically and thermodynamically more favourable than water formation, which is a competing reaction for oxygen removal. Carbon monoxide is also a participant in shift reactions which are catalyzed by alkali present in the ash fraction of coal. A proposed carbonate - bicarbonate - formate mechanism involves generation of hydrogen which can react with aromatic components. Finally, carbon monoxide reduces carboxyls, aldehydes and ketones to form phenols and ethers.

Low ranking coals may contain up to forty per cent moisture, bound in coal particle pores. As the material is heated during liquefaction, the pressure created by vapourizing water in the pores causes the coal particles to break up, thereby exposing more surface for hydrogenolysis. Water also participates in the shift reaction to produce in-situ hydrogen.

Liquefaction may be economically more advantageous if low rank coals are used as feedstock rather than higher rank coals. Oxygenated materials are highly reactive due to the presence of hydroaromatic structures and humic materials which may act as hydrogen donors to stabilize free radical intermediates. Consequently, sixty to seventy per cent of the original material can be converted in minutes. Therefore, space time yields using oxygenated coals may be greater than when higher rank coals are hydrogenolyzed. This would result in lower capital and operating costs. As well, since carbon monoxide is beneficial for converting oxygenated compounds, synthesis gas may be used for the reaction rather than pure hydrogen, which is more costly.

4.2 Coal Pretreatment

4.2.1 Particle Size Reduction

To avoid mass transfer limitations, coal is normally pulverized to minus 100 mesh (Tyler designation) prior to conversion. However, such a small particle size may not be required for lignite hydrogenolysis. It has been shown that lignite particles of minus 100 to minus 2½ mesh produce similar yields after a 30 minute reaction time (Severson, Feb. 1976). Whether particle size would affect conversions at shorter residence times was unclear.

4.2.2 Air Exposure

Table 7 shows the results obtained (Appell et al., 1977) from hydrogenolysis after 11 recycles using both fresh and aged lignite. Air exposure with drying lowered product oil yields from 87% to 78% on a moisture and ash free (maf) basis and increased the viscosity of the liquid products. These results apparently conflict with findings of another study (Severson, Feb. 1976) which showed that storing lignite for up to 36 weeks while exposed to air did not significantly affect product yields from liquefaction. However, the filterability of the solid liquid slurry produced from aged lignite decreased in comparison with the product obtained from freshly ground material. The results of a subsequent study (Severson, July 1976) which are presented in Table 8 show that air exposure lowered liquid oil yields from 66% obtained with fresh lignite to 57.6% (maf basis). Storage under nitrogen or water did not seem to affect conversions.

The results mentioned above show that for a lignite liquefaction process, milling should occur immediately prior to introduction in the reactor. Storage of lignite in lumps rather than in a milled form will significantly reduce the surface area exposed to air.

4.2.3 Oxygen Removal

Oxygen may be removed from coal prior to conversion by carbonization or treatment with base.

Nearly 90% of the oxygen can be eliminated from lignite and peat by heating the material in an inert atmosphere at 570 to 670 K (Warren et al., 1940). However, as shown in Table 9, pre-carbonization decreases oil yields by as much as 50%, and pre-carbonization

Table 7: Comparison between fresh and aged lignite conversion[1]

Parameter[2]	Freshly Ground[3] Lignite	Aged Lignite[4]
Conversion (%)	87	78
Liquid Oil Yield (%)	54	29
Kinematic Viscosity		
at 333 K (cs)	598	12800
at 355 K (cs)	110	1030

[1] from Appell et al. (1977)

[2] after 11 recycles, moisture and ash free lignite basis
reaction conditions - residence time : 1 hour
temperature : 700 K
CO/H_2 ratio : 1/1
pressure : 21 MPa
water/coal/oil ratio: 9/30/70

[3] North Dakota lignite (Zap mine, 29.5% H_2O, 9.0% ash)

[4] North Dakota lignite (Beulah mine, 20.3% H_2O, 7.3% ash), plant grind

Table 8: Effect of lignite storage on hydrogenolysis yields[1]

Storage Medium[2] :	none	nitrogen	nitrogen	air	water
Yields (weight per cent of maf lignite)					
total gas	35.4	28.8	33.7	35.1	33.8
total liquid oil	66.0	67.7	61.4	57.6	66.7
light oil	20.7	16.6	19.7	20.5	22.3
middle oil	45.3	51.1	41.7	37.1	44.4
total water[3]	-10.3	-8.3	-1.8	-5.1	-7.9
unconverted	8.9	11.8	6.7	12.4	7.4

[1] from Severson (July 1976)

[2] stored for 70 weeks

[3] negative signifies water consumption

Table 9: Results of liquefaction of carbonized lignite[1]

Carbonization[2] Temperature K	Solvent	Yield, Weight % maf Lignite					
		Gas	Total Liquid Oil	Light Oil	Middle Oil	Water[5]	Unconverted
none	[3]	38	68	15	53	-13	7
533	[3]	44	64	25	39	-15	7
588	[3]	40	61	10	51	-10	9
643	[3]	33	57	12	45	-8	18
643	[4]	52	35	13	22	-15	28
648	[4]	28	37	4	33	23	12
668	[4]	24	39	10	29	23	14

[1] from Severson (Feb. 1976)

[2] carbonized for 0.5 hours

[3] carbonized with anthracene oil

[4] carbonized without solvent

[5] negative signifies water consumption

at temperatures greater than 588 K also decreases conversion (Severson, Feb. 1976). A mild carbonization (533 K) before hydrogenolysis seemed to increase the light oil yield.

Pre-treatment of the raw material with caustic solution at 570 to 620 K was also found to substantially decrease the oxygen content in lignite (Kasehagen, 1937).

4.2.4 Neutralization

Bases in coal stabilize polymerization and a mesophase formed during liquefaction, which both tend to produce lower liquid yields. Therefore, the addition of acids to neutralize basic constituents in brown coal was found to improve conversions (Storch, 1963). Furthermore, lower viscosity oils were produced when formic acid was added to the solvent used for hydrogenolysis (Appell et al., 1977).

Phenol pretreatment of lignites increased liquid oil yields and conversions (Severson, Feb. 1976). This was attributed, however, to the phenol inducing swelling of the coal thereby facilitating dissolution in the solvent, rather than a chemical phenomena.

The addition of sulphuric acid was required for the liquefaction of brown coals when molybdenum oxide was used as catalyst (Donath, 1963). The acid neutralized calcium humates and formed calcium sulfate. This procedure was not required when iron catalysts were employed.

4.2.5 Dehydration

The removal of water from lignite may have economic benefits. A lower weight per volume would reduce transportation costs and the absence of water vapour would lower operating pressures and decrease formation of carbon dioxide.

Work was conducted to study the effect of dehydration of lignite on conversions (Severson, Feb. 1976). Prior to liquefaction, the lignite and solvent were heated at 488 K in an autoclave. The results showed that lower liquid yields and conversion were obtained. Whether replacing water vapour during the reaction would restore yields and conversion was suprisingly, not studied. However, this is unlikely since the physical action of vapourizing water in the pores breaking up the coal particles would not be present.

4.3 Effect of Solvent Type

4.3.1 Physical Properties

It has been known since early coal conversion processes were designed that the vehicle solvent tended to favour depolymerization reactions and the formation of colloidal solutions. The best solvents for this purpose were organic liquids having a high boiling point and a medium dielectric constant (Storch, 1963).

One of the most effective solvents for the extraction and dissolution of bituminous and brown coals was a mixture of tetrahydronaphthalene, phenol and naphthalene in a 2/1/2 ratio (Pott et al., 1934). When a 1/1 coal to solvent ratio was used, the optimum extraction temperature was between 660 and 680 K. It is likely that hydrogen transfer occurred from solvent to coal constituents during the dissolution process.

The extract yield from a bituminous coal was found to be correlated with the solubility parameter of the solvent. The solubility parameter is a measure of the cohesive forces in a regular solution, which is a solution having a vanishing excess entropy of mixing at constant temperature and volume. The solubility parameter is defined as follows:

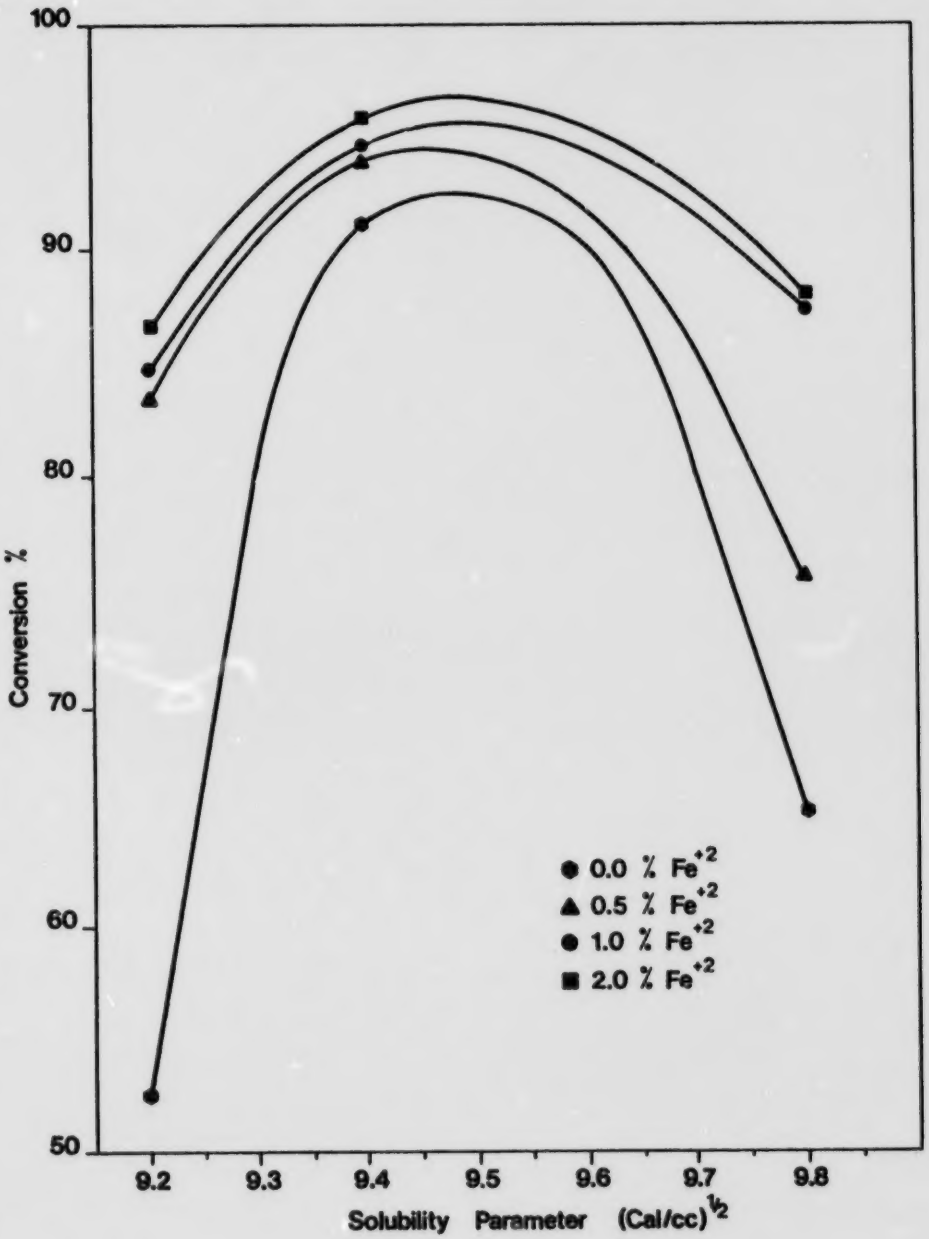
$$\delta^2 = \frac{\Delta U}{v}$$

where δ is the solubility parameter
ΔU is the energy change upon isothermal vapourization of the saturated liquid to the ideal gas state
v is the molar volume of the solvent

Figure 5 shows that optimum conversions of a sub-bituminous coal using impregnated ferrous catalysts were obtained with a solvent having solubility parameter 9.5 (Pastor et al., 1970). Reaction conditions were 714 K temperature, 13.9 MPa initial hydrogen pressure and three hours residence time. Similar correlations were found using various solvents and having both conversion and liquid oil yield as dependent variables (Angelovitch, 1970).

The above results are fundamentally important since the activity coefficient of a regular solution is a function of the solubility parameters. Therefore, the results indicate that yields from liquefaction may be controlled not only by kinetic constraints, but also by thermodynamic constraints.

Figure 5
Effect of Solubility Parameter on Coal Liquefaction (from Pastor et al., 1970)



4.3.2 Catalyst-Solvent Interaction

Since catalysts and solvents interact during extraction and hydrogenolysis, optimum conversions could be obtained by proper adjustment of the catalyst/coal/solvent ratio. Unfortunately, few have attempted to study this problem.

Early Canadian work with bituminous coals has shown that such interactions may exist (Warren et al., 1939). The results given in Table 10 show that with low catalyst loadings, the addition of solvent increased conversion by as much as 10%. However, when high catalyst loadings (> 1% weight of maf coal) were used, the addition of solvent increased conversions by only 3%.

4.3.3 Hydrogen Donor Properties

The role of solvents in hydrogenolysis reactions goes beyond that of a mere vehicle (or pasting oil). Their hydrogen donor and transfer properties are essential in directing hydrogenolysis towards liquid products rather than gases and solids.

Hydrogen donors are required especially during the early stages of hydrogenolysis to stabilize depolymerized coal fragments which are highly reactive from thermal activation (Neavel, 1976).

During liquefaction with coal-derived solvents, hydrogen donors other than tetrahydronaphthalene are generated in situ (Kang et al., 1977). Solvents containing the most hydrogen attached to carbons at the β position on aromatic rings seemed to produce the highest conversions. This type of hydrogen (called β-H) easily participates in transfer reactions. It was also observed that temperature variations less than 5 K were sufficient to promote coke formation. This was probably due to the competition between thermal cracking leading to coke formation and hydrogen transfer leading to liquid formation.

Finally, studies have shown that hydrogen transfer directly from the solvent is predominant over transfer of gaseous hydrogen dissolved in the liquid phase (Whitehurst and Mitchell, 1977).

4.3.4 Petroleum and Coal Derived Solvents

Any economically viable liquefaction process will probably operate with either recycle oil or a petroleum derived solvent. A priori, the best solvent should have a solubility parameter close to 9.5 and have as many β-hydrogens as possible. However, to this date,

Table 10: Conversion of bituminous coal with tin (II) oxide[1]

Catalyst Concentration (weight SnO) % of maf coal	Conversion without recycle oil as vehicle %	Conversion added recycle oil as vehicle %
0	57.7	66.8
0.0096	63.8	72.7
0.0096	63.6	74.1
0.0951	68.9	79.4
0.0951	69.7	79.5
0.899	75.7	82.1
0.899	75.7	82.4
4.56	80.6	83.3
4.56	80.5	83.7
9.51	80.5	84.4
9.51	80.4	83.6

[1] from Warren et al. (1939)

no systematic characterization of cheaply available solvents has been conducted taking into account both solubility parameter and hydrogen transfer characteristics.

The various coal and petroleum derived liquid cuts which were used as start-up solvents for a pilot-scale liquefaction process at the University of North Dakota are listed in Table 11. Recycle oil was used for steady state operation.

The highest liquid product yields were obtained using carbon black feedstock, anthracene oil and creosote oil. Prior hydrogenation of the solvents did not improve liquid oil yields except when using creosote oil. However, infrared analysis indicated that all solvents were hydrogenated during the conversion process. This suggests that hydrogen transfer groups are present in sufficient quantities in the anthracene oil for optimum oil production but not in the creosote oil.

The highest recoveries of the standard solvent cut present in the reacting mixture were obtained with coal derived solvents; up to 85% of the anthracene oil was recovered. When using as received solvents, a net increase of the standard cut was obtained. This indicates that a portion of the liquid product contributes to a standard cut which could probably be used for recycling.

The sulphur content of the liquid products was higher when petroleum derived solvents were used. Gas yields and water consumption were similar for all tests.

Table 12 shows the progressive increase in product viscosity after five solvent recycles. The increase, which is a drawback for a continuous process, is probably due to a decrease in the standard cut fraction.

Table 11: Possible start-up solvents for the hydrogenolysis of lignites[1]

Coal-Derived Solvents
Raw creosote oil, heavy ends cut
Raw creosote oil, standard solvent cut
Hydrogenated raw creosote oil, heavy ends cut
Hydrogenated raw creosote oil, standard solvent cut
Chilled creosote oil, heavy ends cut
Chilled creosote oil, standard solvent cut
Hydrogenated chilled creosote oil, standard cut
Raw anthracene oil, heavy ends cut
Raw anthracene oil, standard solvent cut
Hydrogenated raw anthracene oil, standard solvent cut
Chilled anthracene oil, heavy ends cut
Chilled anthracene oil, standard solvent cut
Hydrogenated chilled anthracene oil, standard solvent cut
Light creosote oil, as received
Middle-heavy creosote oil, as received
Petroleum-Derived Solvents
Heavy aromatic naphtha, as received
#6 fuel oil, standard solvent cut
#5 fuel oil, as received
#5 fuel oil, standard solvent cut
Aromatic tar, as received
Aromatic tar, standard solvent cut
Carbon black feedstock, as received
Carbon black feedstock, standard solvent cut
Aromatic concentrate, as received
Aromatic concentrate, standard solvent cut

[1] from Severson (Feb. 1976)

Table 12: Increase in viscosity of the product slurry from a continuous liquefaction process[1]

Recycle Number	Brookfield Viscosity (at room temperature) cp
1	2580-4170
2	3570-4080
3	3770-3890
4	3575-4500
5	5864

[1] from Severson (Feb. 1976)
reaction conditions - temperature (K) : 400-407
pressure (MPa) : 21.5-22.8
residence time (min) : 30

4.4 Operating Conditions

From a practical viewpoint, a low viscosity product is necessary for further work up and handling. A correlation between viscosity and reaction temperature is given as Figure 6 (Appell et al., 1977). Reaction conditions were 20.8 MPa pressure, one hour residence time at reaction temperature, and feed of 1/1 carbon monoxide to hydrogen and 0.43/1 lignite (mf) to anthracene oil. The results show that a reaction temperature of about 700 K is required to produce a middle viscosity (55 cs) oil that can be recycled. This figure also shows that there is a greater gas consumption at higher temperatures.

A particular distillate cut from the liquid products may be preferable for recycling rather than a portion of the whole product mixture. In this way, the viscosity of the recycle stream can be chosen to suit the particular process.

4.5 Kinetic Aspects

4.5.1 Development of Kinetic Models

The first kinetic model tested for coal conversion involved a simple mechanism represented as follows (Weller et al., 1950):

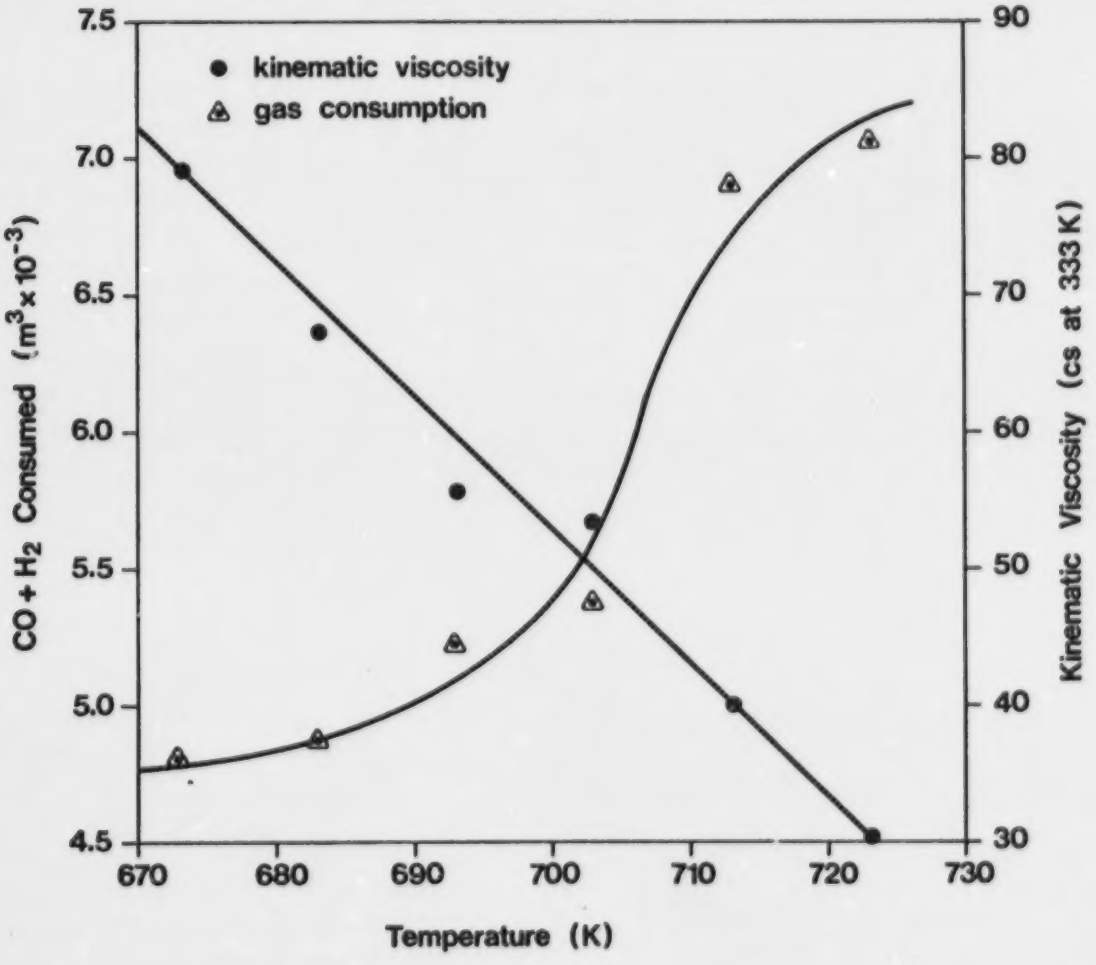
$$\text{coal} \xrightarrow{k_1} \text{asphaltenes} \xrightarrow{k_2} \text{oils}$$

Coal is first transformed to intermediate compounds called asphaltenes which are then converted to oils. Both reactions are first order. The model, which was successfully applied to catalyzed coal conversions in the absence of a vehicle solvent, did not take into account the gases formed from product decomposition.

The model was extended to the case where a hydrogen donor solvent is present in the reaction mixture (Curran et al., 1966). The model predicted that conversion to oils occurs through a dissolution step followed by hydrogen transfer from solvent to thermally activated coal constituents. A mechanism was proposed involving free radicals and catalysis of only hydrogenation of the solvent. Hydrogenation of coal was postulated to occur indirectly from the gas phase to the catalyst, then to the solvent and eventually to the coal. Hydrodynamic factors and catalytic activity of the ash were taken into account in a further extension of the model (Wen and Han, 1975; Han et al., 1978).

Figure 6

Viscosity and Gas Consumption vs Reaction Temperature (from Appell et al., 1977)



A second simple model was applied to the hydrogenolysis of brown coals with a vehicle solvent (Maekawa et al., 1977). The model which involved two competing reactions was represented as follows:

(i) coal $\xrightarrow{k_1}$ oils

(ii) coal $\xrightarrow{k_2}$ asphaltenes $\xrightarrow{k_3}$ oils

A sequence of elementary steps involved in coal liquefaction was postulated as follows (Neavel, 1976):

a. physical break-up of coal particles;

b. thermally induced rupture of chemical bonds;

c. competition between autostabilization, recombination and hydrogen transfer reactions;

d. rehydrogenation of the solvent.

Further work in this area has shown that the removal of oxygen, nitrogen and sulphur from coal occurs to a significant extent before hydrogen transfer (Whitehurst and Mitchell, 1977).

4.5.2 Mechanistic Aspects

Based on the past work reviewed so far, certain events can be postulated to occur during coal liquefaction. A coal-hydrogen donor vehicle solvent - catalyst mixture in the presence of a reducing carbon monoxide-hydrogen atmosphere is considered for the reaction. The following events can occur simultaneously or sequentially to convert coal macromolecules to liquid and gaseous products:

a. initial rapid devolatilization and decomposition occur to form carbon dioxide and water;

b. during the initial pyrolytic stages, free radicals are formed; the concentration of free radicals at a given temperature is probably higher for low ranking than for high ranking coals due to the presence of more oxygen, sulphur and nitrogen;

c. carbonium ions are probably formed by thermal activation of terminal groups of varying electronegativities attached to particular carbon atoms; this step may be catalyzed by metal oxides on silica and alumina present in the ash fraction;

d. a solvent having hydrogen donor properties causes hydrogen transfer to chemically active coal fragments (free radicals and carbonium ions), increasing their hydrogen content and initiating cracking;

e. hydrogen from the gas phase is probably adsorbed on the catalyst, then transferred to the solvent and finally to coal components;

f. hydrogen may be generated in situ from reactions between carbon monoxide and alkali involving a carbonate - bicarbonate - formate mechanism and by the shift reaction;

g. oxygen and sulphur are probably scavenged by acidic groups, oxides and sulphides; the presence of transition metals as sulphides and oxides which can be reduced by carbon monoxide are probably the principal reactants in scavenger reactions.

Nitrogen removal is often difficult during primary conversion due to the occurrence of numerous complex competing reactions.

4.6 Catalysts

4.6.1 General Observations

The task of finding a suitable catalyst for primary conversion which will favour the reactions described in the previous section without being easily deactivated by coke, nitrogen or sulphur, is a difficult one. For low ranking coals, no catalyst addition may be preferable if the vehicle solvent is a good hydrogen donor. However, even in this case, certain added catalysts may allow a reduction in temperature and pressure while maintaining product yields.

Heterogeneous catalysts used in coal conversion may be classified in four categories: metal oxides and sulphides; metal halides; transition metals; alkali and alkaline earth metals.

4.6.2 Metal Oxides and Sulphides

Early German Catalysts

For primary conversion, German workers used molybdenum (VI) oxide (MoO_3) impregnated in coals from an ammonium hydroxide solution. Prior neutralization of calcium humates with dilute sulphuric acid was required for optimum conversion. Typical metal concentrations in maf coal ranged from 0.02 to 0.06 per cent by weight (Donath and Hoering, 1977). The MoO_3 was compared to tin catalysts and found to produce greater liquid yields from sub-bituminous and brown coal, but tin catalysts were more active for bituminous coal liquefaction.

Catalyst (MoO_3) regeneration was unsuccessfully attempted by oxidation of the molybdenum in the unconverted residue. Therefore, a scarcity of molybdenum in Germany at that time prompted the development of a process using available iron oxides. Although these compounds were less active than molybdenum, they were not costly and thus could be used in a larger concentration (up to 10 per cent of the coal weight) without being recovered. Neutralization of calcium humates was not required and even interfered with the reaction (Donath and Hoering, 1977).

The vehicle solvent used in this process was a heavy oil which acted mainly as a carrier for the pulverized coal. Its hydrogen donor properties were not documented.

Table 13 presents a summary of the operating conditions and yields obtained from the liquefaction of brown coals (Donath, 1963). Temperatures and pressures were typically high (755 K and 25 to 66 MPa) and liquid oil yields were approximately 60% of the weight of the maf coal feed.

The liquid oil product obtained from primary conversion of brown, sub-bituminous and bituminous coals was used as a feedstock for vapour phase hydrogenation. Initially, an equimolar mixture of MoO_3, zinc oxide (ZnO) and magnesium oxide (MgO) was used as the catalyst for the refining operation. This mixture is presently used for hydrorefining and hydrocracking. Presulphiding the oxides tended to increase catalytic activity.

Superior hydrogenation was obtained with tungsten disulphide (WS_2) prepared by decomposing ammonium sulphotungstate (Donath and Hoering, 1977). Typical reaction conditions and products are given in Table 14. The results show that 90 to 100% conversions can be obtained for hydrorefining, hydrocracking, and removal of heteroatoms.

Table 13: Brown coal liquefaction using iron oxide catalysts[1]

	Central Germany Brown Coal	Rhenish Brown Coal
Pressure (MPa) :	25	66
Temperature (K) :	753-763	747-753
Catalyst (maf coal basis) :	10% bayermasse (red mud)	6% bog iron ore + 1.2% sulphur
Middle Oil Yield (% maf coal) : (distilled at less than 620 K)	52	52
Gas Yield (% maf coal) :	26	25
Asphaltene and Heavy Oil Yield: (% maf coal)	5	8

[1] from Donath (1963)

Table 14: Hydrogenation with tungsten disulphide catalysts[1]

Feed	Process	Product	Conversion %	Temperature K	Pressure MPa	Feed Rate kg L^{-1} h^{-1}
Brown coal middle oil - 18% phenols 4% nitrogen bases 2.5% sulphur	Removal of oxygen, nitrogen and sulphur	Prehydrogenated middle oil	99.5	653	20	1.0
Diisobutene	Hydrorefining	Isooctane	99	489	25	2.0
Naphthalene	Hydrorefining	Decaline	90	609	20	0.9
Paraffins (b.p. 530-590 K)	Hydrocracking	Gasoline	90	681	22	1.0
n-Butane	Isomerization	Isobutane	35	673	20	0.5

[1] from Donath and Hoering (1977)

A hydrogenation product with a higher octane number was obtained when WS_2 was supported on montmorillonite earth (a natural alumina silicate) treated with a 10% solution of hydrofluoric acid. The catalyst was employed at a concentration of 10% by weight of the support for hydrocracking and reforming. The feed for these processes required prior hydrorefining over a nickel sulphide (NiS)-tungsten disulphide catalyst on alumina (25% WS_2 - 3% NiS - 62% Al_2O_3) to remove the organic nitrogen.

Two other catalyst systems were used to further increase the aromatic content of the product: chromium and vanadium oxides supported on activated carbon operating at 770 K and 30 MPa; presulphided zinc, chromium and molybdenum oxides supported on montmorillonite earth treated with hydrofluoric acid, operating at 61 MPa and 770 K. However, the high temperatures caused extensive gasification. Eventually, the operating temperature was lowered to 670 K when the catalysts were supported on synthesized silica-alumina (Donath and Hoering, 1977).

The above mentioned refining catalysts were also used for hydrogenation of coke oven and brown coal tars. Problems were encountered with ash and condensation reactions which deactivated the catalysts.

Contemporary Processes

Contemporary low rank coal conversion processes have emphasized the use of hydrogen donor solvents and hydrodesulphurization catalysts such as cobalt-molybdate on alumina (CoO - MoO_3 - Al_2O_3).

The H-Coal process has been designed to use cobalt oxide - molybdate on γ-alumina to convert sub-bituminous coals to liquid fuels. The hydrocracking activity of the catalyst allows the breaking of C=O bonds existing as links between condensed aromatics (Kang and Johanson, 1977).

A similar process developed by the Gulf Research and Development Corporation utilizes a catalytic mixture comprised of 1% (by weight) CoO, 0.5% nickel oxide (NiO) and 8% MoO_3 supported on Al_2O_3 in a fixed bed reactor (Montagna and McIlvried, 1976). Operating conditions are 687 K temperature, 24 MPa pressure, hydrogen feed of 1781 m^3 per m^3 of feed, and space velocity of 0.9 kg coal per hour per kg catalyst.

In general, alkali promoters deposited on the catalyst have improved catalytic activity during the primary conversion of coal using synthesis gas (Fu and Batchelder, 1977).

The synthoil process for coal liquefaction was originally based on the use of a continuous reactor containing a fixed bed of $CoO - MoO_3 - Al_2O_3$ pellets. However, recent developments have shown that the catalyst becomes deactivated after only 15 days of run time. As well, when the catalyst was replaced with inert ceramic balls, the process converted 90% of maf West Virginia coal having 5.5% sulphur to a liquid product oil having only 0.7% sulphur, at 28 MPa and 920 K (Yavorsky and Akhtar, 1977). Thus, external catalysts were not necessary for primary conversion since the reaction was promoted by turbulence in the reactor and by the indigenous catalysis from inorganics naturally found in coal.

Similarly, no external catalyst was required for converting lignites in the COSTEAM process. The liquid oil product obtained from this process was catalytically upgraded (Severson, July 1976). A $MoO_3 - NiO - Al_2O_3$ catalyst was found to be superior to $CoO - MoO_3 - Al_2O_3$ for upgrading liquid oil produced from lignites (Stenberg, 1976). The catalysts producing the highest yields of light oils and gasoline were found to be presulphided MoO_3 - nickel sulphate ($NiSO_4$) on fibrous alumina and presulphided commercial $MoO_3 - NiO - Al_2O_3$ (HT-100, Harshaw Chemicals). Both catalysts converted 92% of the maf feed but the former ($MoO_3 - NiSO_4 - Al_2O_3$) gave a 64.0% total liquid oil yield and 26.4% light oil (distilled at less than 383 K) yield while the other gave a 59.8% total liquid oil yield and 32.2% light oil yield (Ralston, 1977/78).

Catalyst Deactivation

Metal oxides and sulphides can become deactivated by carbon deposition, sintering and metal deposition (Ruberto et al., 1977). Carbon formed during coking can block active sites on the catalyst. Sintering is caused by steam reacting with alumina. This phenomenon is most pronounced when converting low rank coals due to their relatively high oxygen and moisture content. Metals such as iron, calcium and sodium which are naturally occurring in the ash fraction of coals can be deposited on external catalysts and block the active sites.

4.6.3 Metal Halides

Metal halides are strong Lewis acids which are known to promote the thermal decomposition of oxygenated organic compounds such as ethers and aldehydes (Glass and Hinshelwood, 1929; Hinshelwood et al., 1930). These compounds would thus be expected to catalyze coal hydrogenolysis. This section summarizes the work conducted in this field.

The results of a study on coal hydrogenolysis using various solid phase metal halide catalysts are given in Table 15 (Kawa et al., 1970). The reaction temperature was 683 K at a pressure of 28 MPa. The results indicate that most metal halides are effective hydrogenation catalysts, yielding less than 20% benzene insolubles.

In the absence of a vehicle solvent, catalytic mixtures of tin (II) oxalate (SnC_2O_4) and ammonium chloride (NH_4Cl) were found effective in promoting coal hydrogenation including highly oxygenated coals (Weller et al., 1950).

Molten zinc chloride ($ZnCl_2$) was used in a pilot scale liquefaction plant as part of the Consol "Project Gasoline" (Zeilke et al., 1966). In this process, catalyst recovery is an economic necessity. Leaching studies have shown, however, that ultimate recoveries of 98.5 to 99.7% are possible (Hill et al., 1977/1978).

4.6.4 Transition Metals

Attempts have been made to use transition metals as coal liquefaction promoters either finely dispersed in the reaction mixture or chemically impregnated in the coal structure. Finely dispersed metals were found to deactivate rapidly during coal conversion processes due to extremes in reaction conditions and thus cannot be used economically (Storch, 1963).

Iron, cobalt, nickel and molybdenum were chemically impregnated by ion exchange in lignite and hydrogenolysis was conducted with carbon monoxide-hydrogen mixtures at 672 K and 21 MPa for 30 minutes (Severson, Feb. 1976). The results of this study, which are given in Table 16, show that impregnated transition metals do not substantially affect liquid oil yields or conversion. Both natural and impregnated lignite produced a 68% oil yield and 92 to 93% conversion.

Table 15: Results of coal liquefaction experiments using metal halide catalysts[1]

Catalyst	Catalyst-to-coal weight ratio[2]	Yields, weight-percent of maf coal						
		Organic benzene insolubles	Asphaltene	Heavy oil	Light oil	Hydrocarbon gases	Acid gases and carbon monoxide	Hot water
None	-	37	28	13	6	6	3	7
$NiI_2.6H_2O$	1.0	18	2	21	38	10	4	12
$NiBr_2$	1.0	20	4	29	33	10	6	5
ZnI_2	1.0	10	1	5	55	17	7	10
I_2	1.0	23	1	8	48	15	3	11
$ZnBr_2$	1.0	10	2	8	56	14	3	13
$ZnCl_2$	1.0	12	2	16	45	14	4	11
$SnCl_2.2H_2O$	1.0	18	7	40	29	6	4	1
CdI_2	1.0	17	3	24	37	13	1	12
$FeI_2.4H_2O$	1.0	20	9	13	41	10	2	5
SnI_2	1.0	8	14	42	20	6	5	5
$ZnCl_2$	0.01	33	26	18	8	8	4	7
$SnCl_2.2H_2O$	0.01	12	38	34	7	4	5	7

[1] from Kawa et al. (1970)

[2] does not include water of hydration

Table 16: Hydrogenolysis of lignites impregnated with transition metals[1]

	Raw Lignite	Treated Lignite[2]	
Cations present:	natural	none	transition metals
Yields (weight per cent of maf lignite):			
total gas	38	26	25
total liquid oil	68	64	68
light oil	15	13	20
middle oil	53	51	48
total water[3]	-13	-1	-1
unconverted	7	11	8

[1] from Severson (Feb. 1976)

[2] treated with 1N hydrocloric acid solution reducing the ash content from 10% to 3% (weight of mf lignite)

[3] negative signifies water consumption

4.6.5 Alkali and Alkaline Earth Metals

Alkali and alkaline earth metals are thought to catalyze the liquefaction of oxygenated materials with carbon monoxide by promoting the shift reaction through a formate intermediate (Appell et al., 1972). Although the addition of these metals substantially improved liquid oil yields and conversions from the liquefaction of peat (Cavalier and Chornet, 1977) and cellulosic materials (Appell et al., 1971), no such effect was found during lignite liquefaction, as shown in Table 17 (Severson, Feb. 1976). For both untreated and treated (with impregnated metals) lignite, total liquid oil yields ranged from 62 to 68% (maf lignite) and light oil yields from 13 to 19%. The ash material present in the lignite was obviously sufficient to catalyze the reaction.

Table 17: Hydrogenolysis of lignites impregnated with alkali and alkaline earth metals[1]

	Raw Lignite	Treated Lignite[2]		
Cations present:	natural	none	alkali metals	alkaline earth metals
Yields (weight per cent of maf lignite):				
total gas	38	26	41	30
total liquid oil	68	64	67	62
light oil	15	13	17	19
middle oil	53	51	49	43
total water[3]	-13	-1	-14	0
unconverted	7	11	6	8

[1] from Severson (Feb. 1976)

[2] treated with 1N hydrochloric acid solution, reducing the ash content from 10% to 3% (weight of mf lignite)

[3] negative signifies water consumption

5.0 LIQUEFACTION PROCESSES

5.1 Uncatalyzed Processes

Uncatalyzed processes refer to those where no catalyst is added. This however, does not preclude catalytic activity, since the inorganics present in coal ash may act as in-situ catalysts.

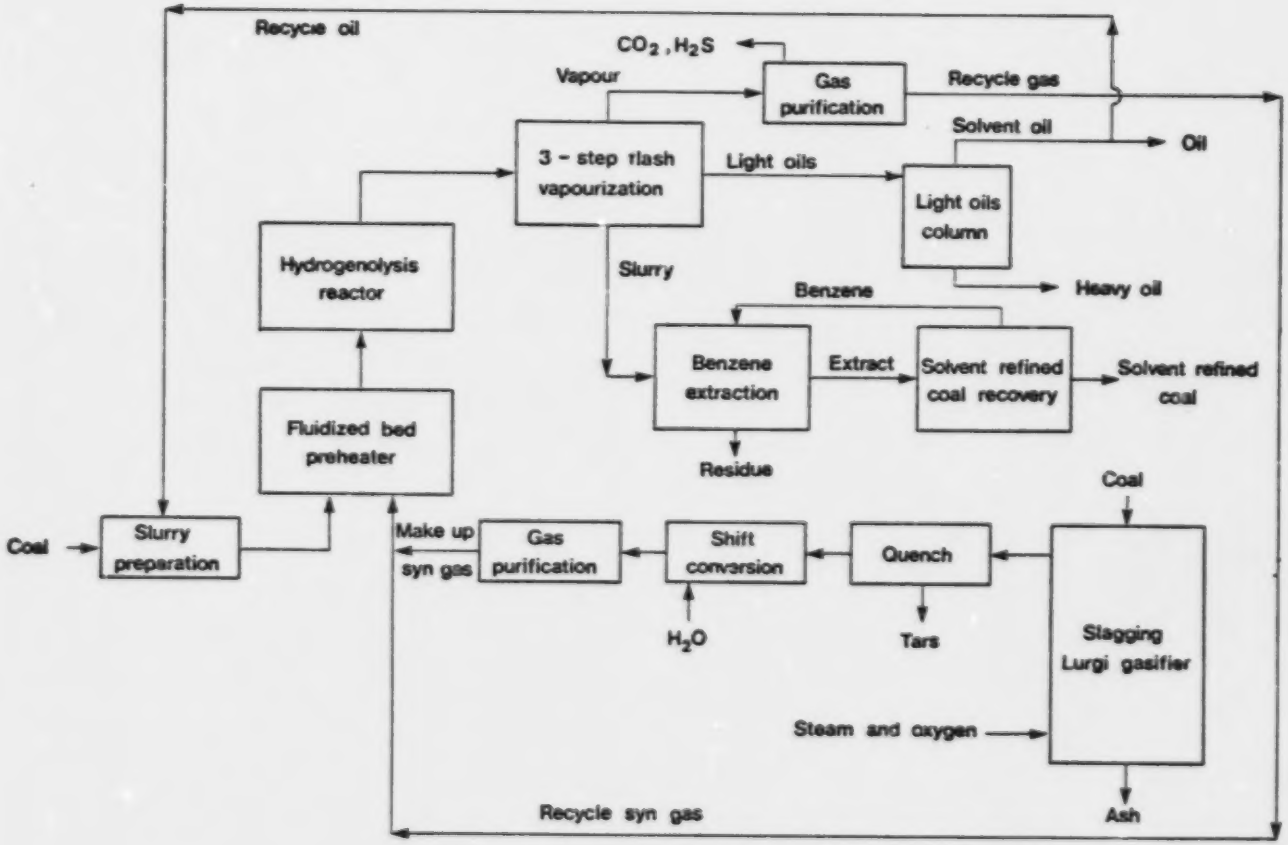
Figure 7 shows the simplified process flowsheet for production of solvent-refined lignite (Baria, 1975). The feed is crushed and pulverized so that 100 per cent passes through a 60 Tyler mesh and 90 per cent passes through a 200 Tyler mesh, and is then blended into a slurry with a recycled, petroleum derived solvent. Recycle gas containing carbon monoxide and hydrogen combined with make-up synthesis gas from a slagging Lurgi gasifier is mixed with the coal slurry and heated to 670 K in a fluidized bed pre-heater. The mixture is then compressed to 21 MPa and sent to the hydrogenolysis reactor where coal depolymerization and reduction reactions occur at 670 K. In the reactor, hydrocarbons, heavy oils, hydrogen sulphide and carbon dioxide are also formed. The mineral content of the coal remains undissociated.

The non-condensable gases and the light oils are separated from the slurry in three flash-vaporization steps during which the pressure is reduced to 2700 Pa. The non-condensable gases consist of carbon monoxide, hydrogen, methane, carbon dioxide, hydrogen sulphide and inerts. This gas is sent through a purification unit where the carbon dioxide and hydrogen sulphide are removed, and the cleaned gas recycled to the hydrogenolysis reactor. A quantity of the gas stream is vented to prevent build-up of inerts within the system. The light oils consist of the original petroleum-derived solvent plus light hydrocarbons and phenols. The solvent is recycled to form a slurry with the coal. To be successful, sufficient solvent must be generated from the coal to maintain the process.

The residue consists of minerals, unreacted lignite and solvent-refined lignite, and is referred to as the vacuum flash bottoms. These are pumped to a mixing vessel at 620 K and mixed with benzene. The mixture is pumped to a gravity settler where the mineral residue is removed and the dissolved solvent-refined lignite and benzene are withdrawn from the top of the settler. Benzene is then removed by flash distillation and recycled. The solvent-refined lignite is solidified and collected.

Figure 7

Simplified Flowsheet for the Solvent Refined Lignite Process



The make-up synthesis gas is obtained from a slagging Lurgi gasifier which operates at 2.9 MPa pressure. The ash is withdrawn as a slag. The slagging gasifier is used because the ratio of carbon monoxide to hydrogen in the exit stream is 3:1, approximately the ratio needed in the main reactor, and thus the gas needs little or no shift conversion. However, the gas is purified to remove hydrogen sulphide and carbon dioxide before entering the hydrogenolysis reactor.

The advantages of this process include:

a. low hydrogen consumption since the coal is not completely hydrogenolysed;

b. the use of any kind of coal, caking or non-caking;

c. no need for pretreatment of coal.

The disadvantages are:

a. an oxygen plant is needed for the slagging Lurgi gasifier;

b. the recovery of the solvent-refined lignite by benzene extraction has not been done on other than laboratory scale.

A process analysis has been carried out for the design of a process development unit (Baria, 1975). The design data for a slagging Lurgi gasifier to produce make-up synthesis gas was obtained from tests run on Velva lignite. The following assumptions were made in the design calculations:

a. the lignite is charged with full moisture content, both to the hydrogenolysis reactor and to the gasifier;

b. the make-up synthesis gas requirement is 0.34 million standard cubic metres per hour;

c. the steam feed rate to the gasifier is 305 kg per 100 kg maf lignite;

d. the oxygen to steam molar ratio is 0.9 in the gasifier;

e. operating pressure in the gasifier is 2.9 MPa;

f. the solvent feed rate is 330 kg per 100 kg maf lignite;

g. all the solvent is recovered and recycled.

The process was designed to produce 284 TJ per day of solvent-refined lignite. Table 18 presents the material and energy balances for the lignite hydrogenolysis section and Table 19 gives the overall energy balance for the solvent-refined lignite process.

The lignite consumption on a daily basis is 8603 Mg for the gasifier, 28,645 Mg for the hydrogenolysis reactor and 454 Mg for steam generation. The solvent circulation rate is 46,641 Mg per day for the reactor, and the benzene circulation rate is 32,817 Mg per day for the extraction of the solvent-refined lignite. The solvent and benzene are both completely recovered in the process and recycled. In addition to the 7,772 Mg per day of solvent-refined lignite, 214 Mg of light oil, 1,282 Mg of wash solvent, 1,046 Mg of heavy oil and 130 Mg of sulphur are produced per day. The heating value of the solvent refined lignite is 36,483 kJ per kg.

The thermal efficiency for the hydrogenolysis section is 75.6 per cent and the overall thermal efficiency for the solvent-refined lignite process is 73.3 per cent.

The COSTEAM process is similar to the solvent refined lignite process. The main differences are that COSTEAM does not contain a benzene extraction step and process conditions are such that the main products are gases and liquid oils rather than a solid fuel.

5.2 Directly Catalyzed Processes

For directly catalyzed processes, hydrogen, solvent, coal and catalyst are simultaneously present in the reactor. The early German Bergius processes clearly belonged in this category.

5.2.1 H-Coal

The H-coal process for conversion of coal into liquid oil products was developed by Hydrocarbon Research, Inc., sponsored by the Office of Coal Research during the period 1965 to 1967. At present, the research program is being supported by Standard Oil of Indiana (Amoco), Atlantic Richfield Company, Exxon Research and Engineering Company and Ashland Oil Company. A 635 Mg per day pilot plant is proposed for construction to confirm and scale-up results from a 2.7 Mg per day process development unit.

Table 18: Material and energy balance for the lignite hydrogenolysis section[1]

	Mg/day	Heat of Combustion TJ/day
Input		
Lignite for hydrogenolysis reactor	28,645	454.4
Make-up synthesis gas	6,446	114.5
Process solvent	48,641	2
Benzene	32,817	2
	116,549	568.0
Output		
Solvent refined lignite	7,772	283.5
Mineral residue	3,540	-
Water	3,715	-
Light oil	214	9.0
Wash solvent	1,282	53.8
Process solvent	48,641	2
Benzene	32,817	2
Heavy oil	1,046	29.1
Sulphur	130	1.7
Vent gases	16,658	52.8
	115,815	429.8

Thermal efficiency for hydrogenolysis = $\frac{429.8}{568.9} \times 100 = 75.6\%$

[1] from Baria (1975)

[2] the heat of combustion of the process solvent and benzene is not taken into account since they are assumed to be recovered in the process.

Table 19: Overall energy balance for the solvent refined lignite process[1] (including slagging Lurgi gasifier)

	Mg/day	Heat of Combustion TJ/day
Input		
Lignite for gasifier	8,603	136.4
Lignite for hydrogenolysis reactor	28,645	454.4
Lignite for steam and power generation	454	7.2
	37,702	598.0
Output		
Solvent refined lignite	7,772	283.5
Mineral residue	3,540	-
Light oil	214	9.0
Wash solvent	1,282	53.8
Heavy oil	1,046	29.1
Vent gases from hydrogenolysis reactor	16,658	52.8
Sulphur	150	2.4
Ash	533	-
Tar	215	8.0
	31,410	438.6

Overall thermal efficiency = $\frac{438.6}{598.0} \times 100 = 73.3\%$

[1] from Baria (1975)

A simplified flowsheet for the H-Coal process is shown in Figure 8 (Baria, 1975). The coal is dried and pulverized to 40 mesh, and slurried with recycle oil. The coal-oil slurry is mixed with recycle and make-up hydrogen, pressurized to 15.7 MPa and fed to a preheater operating at 725 K. From the preheater the coal slurry and hydrogen are fed to the bottom of the hydrogenator which contains a bed of fluidized catalyst, normally cobalt molybdate. The reactor is operated at 17 to 19 MPa and 700 to 730 K.

The vapours from the reactor are scrubbed with a medium volatility oil in the recycle gas scrubber. Light hydrocarbons are removed and the gas containing essentially hydrogen is recycled. The liquid slurry exits from the top of the reactor at reaction temperature and pressure and is flashed to atmospheric pressure. The vapours from the atmospheric flash drum which consist of carbon monoxide, carbon dioxide, hydrogen sulphide and hydrocarbons are sent to gas purification to remove hydrogen sulphide and carbon dioxide. The hydrocarbon-rich stream may be supplied to an oil refinery as a gas of high calorific value. The liquid slurry from the atmospheric flash drum which consists of unreacted coal, ash and synthetic crude oil is flashed in a vacuum drum to obtain a vacuum-overhead distillate which is the synthetic crude oil and a vacuum-bottoms slurry. A part of the vacuum-overhead distillate oil is recycled to the coal slurry preparation area.

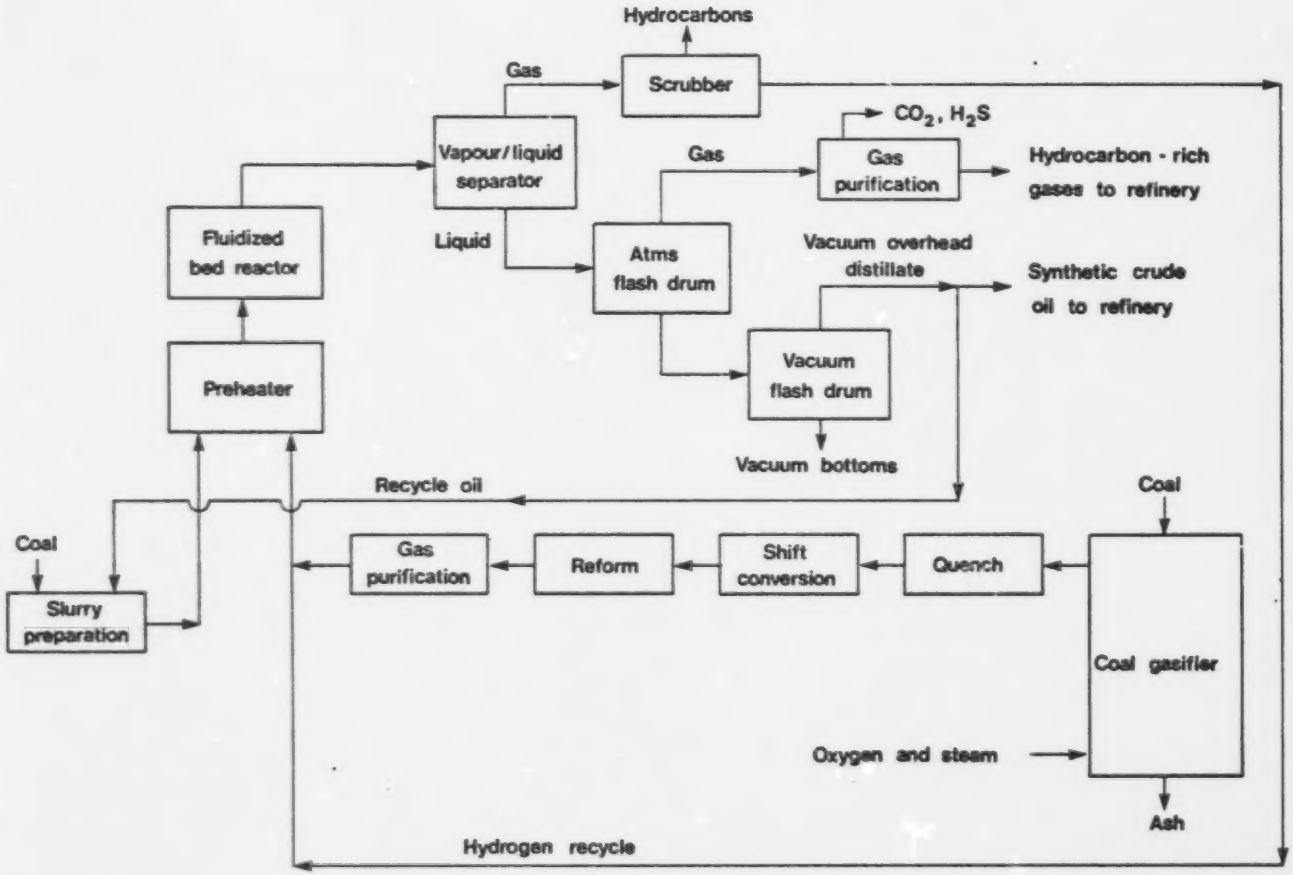
The H-Coal process can be operated to produce a synthetic crude oil which can readily be processed to yield gasoline with 100+ octane rating. It can also be operated under milder conditions with less hydrogen consumption to produce a low sulphur fuel oil.

The H-Coal process requires 440 to 625 standard cubic metres of hydrogen per Mg of coal processed depending on the type of crude oil produced. The hydrogen is produced by gasification of the coal, but can also be produced by steam reforming of the hydrocarbon-rich gases or by gasification of the vacuum bottoms which are added to the coal.

H-Coal differs significantly from the others in that it uses a back-mixed reactor. This makes it less suitable if a high degree of conversion is required but on the other hand makes it very desirable as a first stage treatment to stabilize the coal derived substance and to reduce its tendency to coking. If followed by a second stage fixed bed catalytic reactor in a plug-flow regime, a high level of conversion to synthetic crude or even to gasoline is possible.

Figure 8

Simplified Flowsheet for H-Coal Process



The advantages of this process include:

a. simple process;

b. use of any type of coal;

c. possible synthesis of a wide variety of products by varying pressures and temperatures;

d. ability of present day refineries to process the synthetic crude oil produced;

e. high thermal efficiency.

The process suffers from the fact that it requires a hydrogen generation facility.

Design calculations for the H-Coal process were based on the data obtained in laboratory tests with lignite from Stark County, North Dakota and Wyodak sub-bituminous coal from Wyoming (Baria, 1975). The following assumptions were made:

a. all make-up hydrogen required for the hydrogenation step is produced by gasification of lignite with steam and oxygen; the raw gas is shifted, the methane is steam reformed to hydrogen and the gas purified to yield pure hydrogen;

b. steam requirement for gasification is 820 kg per 1000 kg as received lignite used for gasification;

c. oxygen requirement for gasification is 230 kg per 1000 kg as received lignite used for gasification;

d. make-up hydrogen requirement for hydrogenation is 737 standard cubic metres per Mg maf lignite;

e. oil recirculation rate is 600 kg per 1000 kg dry lignite;

f. yield of synthetic crude oil is 50 L per kg maf lignite;

g. the calorific value of the synthetic crude oil is 45,400 kJ per kg.

Design capacity of the process is 284 TJ per day equivalent of synthetic crude oil. The material and energy balances for the coal hydrogenation process are given in Table 20 and the overall energy balance for the H-Coal process is given in Table 21. The lignite consumption on a daily basis is 25,143 Mg for hydrogenolysis, 9,924 Mg for hydrogen generation, and 4,536 Mg for steam and power generation. The daily production is 6,234 Mg or 6.98 ML of synthetic crude oil, 4,328 Mg or 2.6 x 10^{12} standard cubic metres per day of hydrocarbon-rich gas, 178 Mg of sulphur, 135 Mg of ammonia and 4,511 Mg of char. The overall thermal efficiency is 77.7 per cent.

5.2.2 Synthoil

The Synthoil process was developed under sponsorship of the Energy Research and Development Administration. A 450 kg per day unit was operated for process development and a 900 kg per day pilot plant has been in operation since 1976.

A simplified flowsheet for the Synthoil process is shown in Figure 9 (Baria, 1975). The coal is crushed, pulverized, slurried (43 percent solids) with recycled oil and then fed into a fixed bed catalytic reactor at pressures between 14 and 28 MPa, a temperature of 730 K and a residence time of 10 minutes. The catalyst used is cobalt molybdate on activated silica formed into 3 mm pellets. The hydrogen requirements are supplied by feeding into the reactor a mixture of hydrogen rich recycle gas and a make-up stream. The effluent from the reactor is separated into vapour and liquid streams in a vapour-liquid separator.

The vapour stream consists of the unreacted hydrogen, carbon monoxide, carbon dioxide, gaseous hydrocarbons, light oils, hydrogen sulphide and water vapour. The hydrogen sulphide and carbon dioxide are removed in an acid gas purification step. The gases are cooled to condense the light oils, water and ammonia and then fractionated to recover hydrogen for recycling. The hydrocarbon-rich gases can be used for hydrogen production.

The liquid stream containing unreacted coal, ash and oil from the vapour-liquid separator is centrifuged to recover oil, part of which is recirculated. The solid residue is pyrolyzed to obtain more oil, a carbonaceous residue which contains 75 per cent ash, and some hydrogen and methane.

Table 20: Material and energy balance for the H-coal process[1] (excluding hydrogen generation)

	Mg/day	Heat of Combustion TJ/day
Input		
Lignite for hydrogenolysis	25,143	398.8
Hydrogen gas	911	126.1
	26,054	524.9
Output		
Synthetic crude oil	6,234	283.8
Unreacted ash-free lignite	1,559	43.7
Ash	2,953	-
Steam	11,959	-
Sulphur	146	1.9
Ammonia	135	3.1
Hydrocarbon-rich gas	4,328	149.8
	27,314	482.3

Thermal efficiency for hydrogenolysis process = $\frac{482.3}{524.9} \times 100 = 91.9\%$

[1] from Baria (1975)

Table 21: Overall energy balance for the H-coal process[1] (including hydrogen generation)

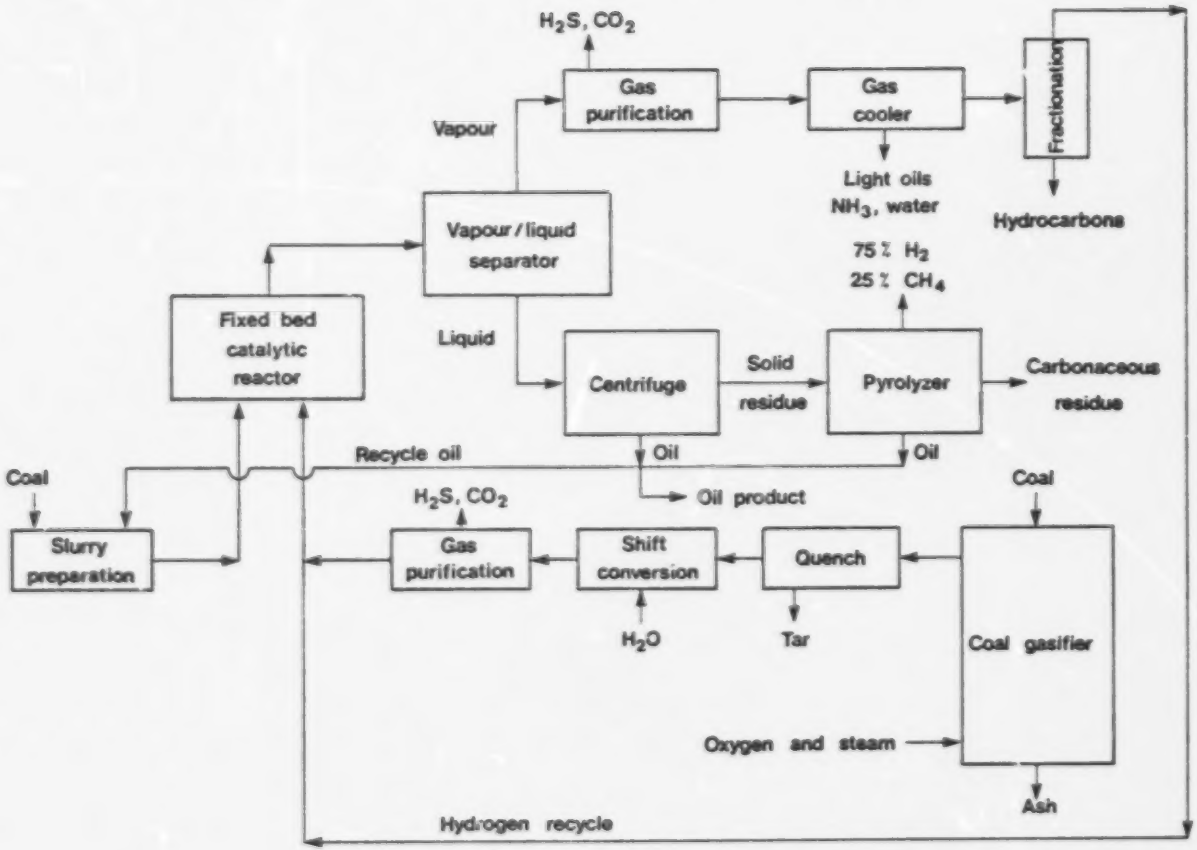
	Mg/day	Heat of Combustion TJ/day
Input		
Lignite for hydrogenolysis	25,143	398.8
Lignite for gasification	9,924	157.2
Lignite for steam generation	4,536	72.0
	39,603	628.0
Output		
Synthetic crude oil	6,234	283.8
Unreacted ash-free lignite	1,559	43.7
Tar	136	5.1
Sulphur	178	2.4
Ammonia	135	3.1
Hydrocarbon gases	4,328	149.8
	12,570	487.9

Overall thermal efficiency = $\frac{487.9}{628.0}$ X 100 = 77.7%

[1] from Baria (1975)

Figure 9

Simplified Flowsheet for Synthoil Process



The make-up hydrogen for the process can be generated by reacting coal and the residual char with steam and oxygen in a gasifier. Hydrogen can also be obtained by reforming the hydrocarbon-rich gases with steam.

The reactor has a large length/diameter ratio and thus requires a high superficial velocity to maintain turbulence. A consequence is a high pressure drop through the reactor.

The advantages are that the process can use any coal and is relatively simple to operate. However, a hydrogenation facility is required, an oxygen plant is necessary and coal consumption is high if all the hydrogen is synthesized from coal.

Design calculations for the Synthoil process have been based on available data for Wyoming sub-bituminous and Kentucky bituminous coals (Baria, 1975) for a process to produce an equivalent of 284 TJ per day of oil. The following assumptions were made:

a. all the make-up hydrogen required for hydrogenolysis is generated by gasification of lignite using steam and oxygen, shifting the gases, and removing the hydrogen sulphide and most of the carbon dioxide;

b. steam requirement for the gasifier is 820 kg per 1000 kg as received lignite;

c. oxygen requirement for the gasifier is 230 kg per 1000 kg as received lignite;

d. make-up hydrogen requirement is 80 kg per 1000 kg as received lignite used for hydrogenolysis;

e. amount of oil produced is 335 kg per 1000 kg as received lignite used for hydrogenolysis;

f. the carbonaceous residue contains 75 per cent ash;

g. the oil recycle rate is 1,297 kg per 1,000 kg as received lignite used for hydrogenolysis;

h. the calorific value of the oil is the same as that obtained from Wyoming sub-bituminous coal (36,000 kJ/kg).

The material and energy balances for the hydrogenolysis process are given in Table 22. The overall energy balance for the complete process including hydrogen generation is given in Table 23. The daily lignite consumption is 23,499 Mg for hydrogenolysis and 26,551 Mg for hydrogen generation to produce 7,870 Mg of oil per day. The by-products are 172 Mg of ammonia, 231 Mg of sulphur, 296 Mg of light oil, 1,943 Mg of carbonaceous residue, 363 Mg of tar and 12,695 Mg of hydrocarbon-rich gas. This hydrocarbon-rich gas consists of 20 per cent carbon monoxide and 50 per cent methane plus other hydrocarbons and has a heating value of 21.1 MJ per standard cubic metre. This gas can be used for hydrogen manufacture by the steam reforming process followed by shift conversion which would significantly reduce coal requirements for hydrogen generation.

The thermal efficiency of the hydrogenolysis process is 74.4 per cent, giving an overall thermal efficiency of 71.1 per cent. The fuel requirement for steam generation is totally obtained from the hydrocarbon-rich gases.

5.2.3. Gulf Process

The Gulf process is proprietary and details have not been released. From the limited amount of published information it appears to use a plug flow fixed bed reactor into which hydrogen and a slurry of pulverized coal are fed. Details on the separation of oil from solid residue are not available.

5.3 Indirectly Catalyzed Processes

In the indirectly catalyzed processes, a hydrogen-donor solvent is used to extract coal. During the extraction step, hydrogen is transferred from solvent to extracted coal. The hydrogen depleted solvent is subsequently hydrogenated in the presence of a catalyst to regenerate its hydrogen-donor capacity. The extraction step is usually at a moderate pressure and gaseous hydrogen is not present in the hydrogenolysis reactor. Typical of this approach are the Consol Synthetic Fuel process, Exxon's Donor Solvent process and Pittsburg and Midway Coal Mining's COG process.

Table 22: Material and energy balance for the Synthoil process[1] (excluding hydrogen generation)

	Mg/day	Heat of Combustion TJ/day
Input		
Lignite for hydrogenolysis	23,499	372.4
Hydrogen-rich gas	12,240	366.1
	35,739	738.5
Output		
Oil	7,870	283.8
Carbonaceous residue	1,943	7.9
Water	11,910	-
Ammonia	172	4.0
Sulphur	146	1.9
Light oil	296	12.3
Pyrolysis gas	123	10.4
Hydrocarbon-rich gas	12,695	228.9
	35,155	549.2

Thermal efficiency for hydrogenolysis = $\frac{549.2}{283.8}$ X 100 = 74.4%

[1] from Baria (1975)

Table 23: Overall energy balance for the Synthoil process[1] (including hydrogen generation)

	Mg/day	Heat of Combustion TJ/day
Input		
Lignite for gasification	26,551	421.0
Lignite for hydrogenolysis	23,499	372.4
	50,050	793.4
Output		
Oil	7,870	283.8
Carbonaceous residue	1,943	7.9
Ammonia	172	4.0
Sulphur	231	3.1
Light oil	296	12.3
Pyrolysis gas	123	10.4
Hydrocarbon-rich gas	12,695	228.9
Tar	363	13.5
	23,693	563.9

Overall thermal efficiency = $\frac{563.9}{793.4} \times 100 = 71.1\%$

[1] from Baria (1975)

5.3.1 Consol Synthetic Fuel Process

The Consol Synthetic Fuel (CSF) process was developed by Consolidated Coal Corporation in 1963 with the Office of Coal Research to produce liquid fuels from coal. In 1967 an 18 Mg per day coal hydrogenolysis pilot plant was constructed and operated at Cresap, West Virginia. The Cresap pilot plant did not achieve satisfactory performance during its 40 months of operation, and the plant was shut down in April 1970. Although the process appeared to be technically and economically feasible, the plant was operated for less than 500 hours and insufficient data was collected to permit detailed design of a commercial plant. An engineering evaluation of the pilot plant was made, and numerous recommendations proposed regarding renovation and operational changes to obtain information needed for design of a commercial scale plant. In May 1974, the Office of Coal Research awarded a contract to Fluor Incorporated to reactivate the Cresap pilot plant.

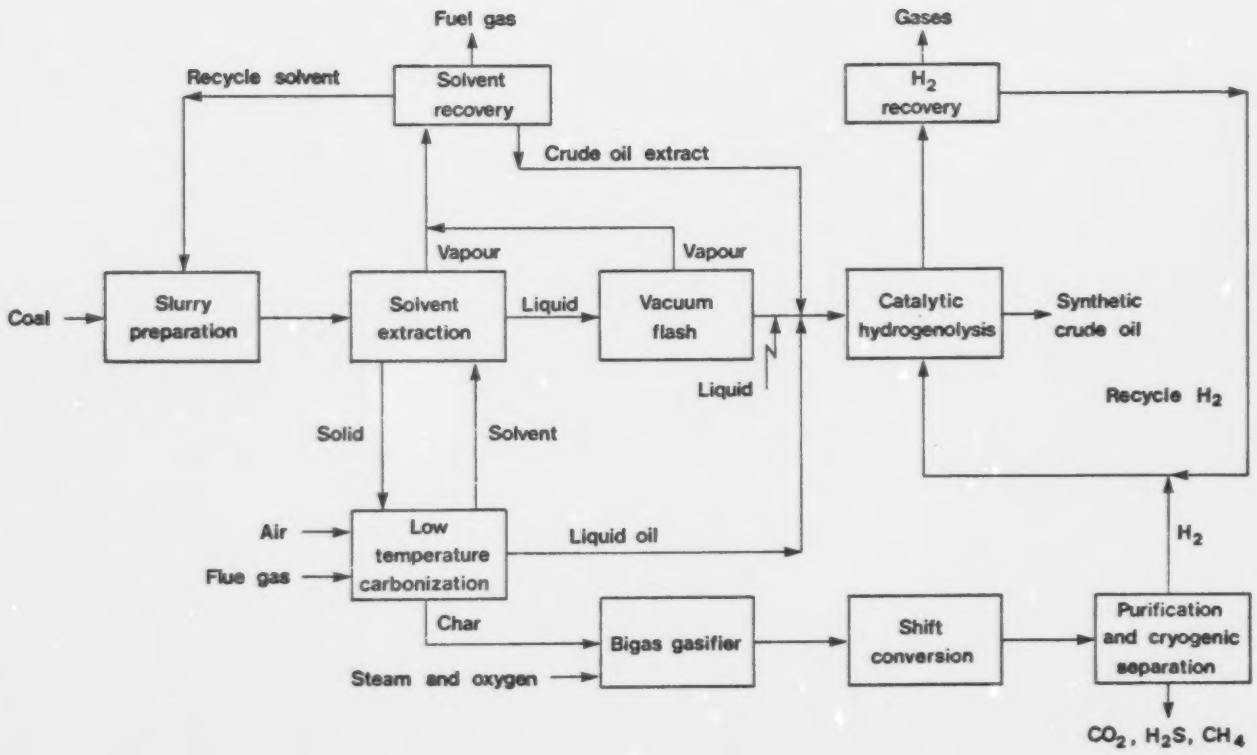
A simplified flowsheet of the CSF process is shown in Figure 10 (Baria, 1975). The coal is dried and crushed so that 99 per cent of the coal passes through 8 mesh and then slurried with 2.5 parts (to 1 part moisture free coal) of hydrogen donor solvent (530 K to 700 K middle distillate oil) obtained from the process. The slurry is preheated to 700 K and then fed to a stirred-stage extractor with a residence time of 30 minutes, temperature of 670 K and pressure between 1.1 and 2.9 MPa. The extraction step depolymerizes and stabilizes the coal. The gas, water vapour and light oil vapours are separated, condensed and recovered.

The liquid slurry is cooled to 600-630 K depressurized to 1.1 MPa and the off-gases collected. The unextracted coal and ash are separated from the slurry in liquid hydrocyclones. The solid residue in a concentrated slurry (40 per cent solids) is sent to a low-temperature carbonization unit. The solvent is recovered and additional liquid-fuel products and fuel gas are obtained. The high-ash char from the carbonization unit is used for hydrogen generation.

The liquid overflow from the hydrocyclones containing the extracted coal and solvent is flashed at 40 to 90 kPa and 590 K. The overhead vapour is distilled to obtain light oil, water and hydrogen deficient oil, which is recycled to mix with coal.

Figure 10

Simplified Flowsheet for CSF Process



The flash underflow containing 15 to 35 per cent solvent is fed to the hydrogenolysis section consisting of three reactors in series. Total residence time is five hours. The reactors are operated at 700-730 K, 24 MPa, with a recycled and make-up hydrogen feed. The catalyst used comprises 1.5 mm beads of cobalt-molybdenum-nickel on an alumina base. Liquid products are flashed overhead, cooled, condensed and separated from the gas. The gases are compressed, the hydrocarbons liquefied and separated, and the non-condensable hydrogen is recycled.

The condensed vapours from the extraction step are sent to a recovery unit where the solvent is removed as overheads in a fractionating column, and the synthetic crude oil is obtained as bottoms.

Hydrogen is generated by gasification of the char from the carbonization unit in the presence of oxygen and steam in a Bigas reactor. The effluent gas is quenched, shifted, purified to remove acid gases and carbon monoxide, and sent to the hydrogenolysis unit. The products from the CSF process are synthetic crude oil, naptha and gas of high calorific content.

The process contains the following features:

a. in-situ generation of hydrogen from char produced in the process;

b. high thermal efficiency;

c. usage of any type of coal;

d. formation of a variety of products including naphtha and gases of low and high calorific values.

However there are serious problems involved with the solid-liquid separations, and an oxygen plant is required for hydrogen generation.

Data from the processing of a West Virginia bituminous coal was used for the following description of design criteria (Baria, 1975). No data was available for using lignite. The basic process design produces 284 TJ per day equivalent of 42,000 kJ per kg synthetic fuel oil.

The following assumptions were made:

a. lignite with its full moisture content is charged to to the system;

b. the recycle solvent requirement is 250 kg per 100 kg maf lignite;

c. the recycle hydrogen requirement is 1.74 million standard cubic metres per Mg extract;

d. oxygen requirement for the char gasifier is 74.3 kg per 100 kg maf char;

e. calorific value of the synthetic fuel oil product is 42,000 kJ per kg.

The material and energy balances for the process, including hydrogen generation, are given in Table 24. The overall energy balance for the process, taking into consideration that carbonization flue gases and the liquefaction residue are used for generating power, is shown in Table 25. The lignite consumption for the process is 33,673 Mg per day with an additional 4,536 Mg per day needed for steam and power generation. The products from this process on a daily basis are 6,778 Mg of synthetic fuel oil, 1,985 Mg of high heat content hydrocarbon-rich fuel gas, 1,752 Mg naphtha, 210 Mg sulphur and 248 Mg ammonia. The thermal efficiency of the process is 92.6 per cent while the overall thermal efficiency is 77.1 per cent when part of the energy produced is used for power generation.

5.3.2 Coal-Oil-Gas

The Coal-Oil-Gas (COG) process is expected to be economically feasible since, in making oil from coal, gas is produced and solvent refined coal may be synthesized and used as a fuel for plant operations. The economic evaluation and process design of such a COG refinery was done by Chem Systems for the Pittsburg and Midway Coal Mining Company using a combination of the Solvent Refined Coal, H-Coal and Bigas processes (Baria, 1975). A simplified flow diagram of the process is shown in Figure 11.

Approximately 75% of the dried, crushed coal feed is transformed to solvent refined coal. The process solvent is recovered and recirculated, light liquids are hydrotreated and the unconverted residue is sent to a Bigas unit. Part of the solvent-refined coal is used internally as fuel for the refinery, part is sent to the hydro-conversion unit for transformation into a liquid fuel, and part sold as by-product.

Table 24: Material and energy balance for the CSF process[1] (including hydrogen generation)

	Mg/day	Heat of Combustion TJ/day
Input		
Lignite for process	33,673	534.2
Air for carbonization	4,974	-
Oxygen for Bigas gasifier	3,494	-
Steam for Bigas gasifier	6,792	-
	48,933	534.2
Output		
Synthetic fuel oil	6,778	283.8
Hydrocarbon-rich fuel gas	1,985	95.5
Naphtha	1,752	79.8
Sulphur	210	2.7
Ammonia	248	5.7
Ash	2,087	-
Water	13,836	-
Vent carbon dioxide	13,411	-
Carbonization flue gas	5,860	5.8
Hydrogenation residue	2,321	21.1
	48,488	494.4

Thermal efficiency for process = $\frac{494.4}{534.2} \times 100 = 92.6\%$

[1] from Baria (1975)

Table 25: Overall energy balance for the CSF process[1]

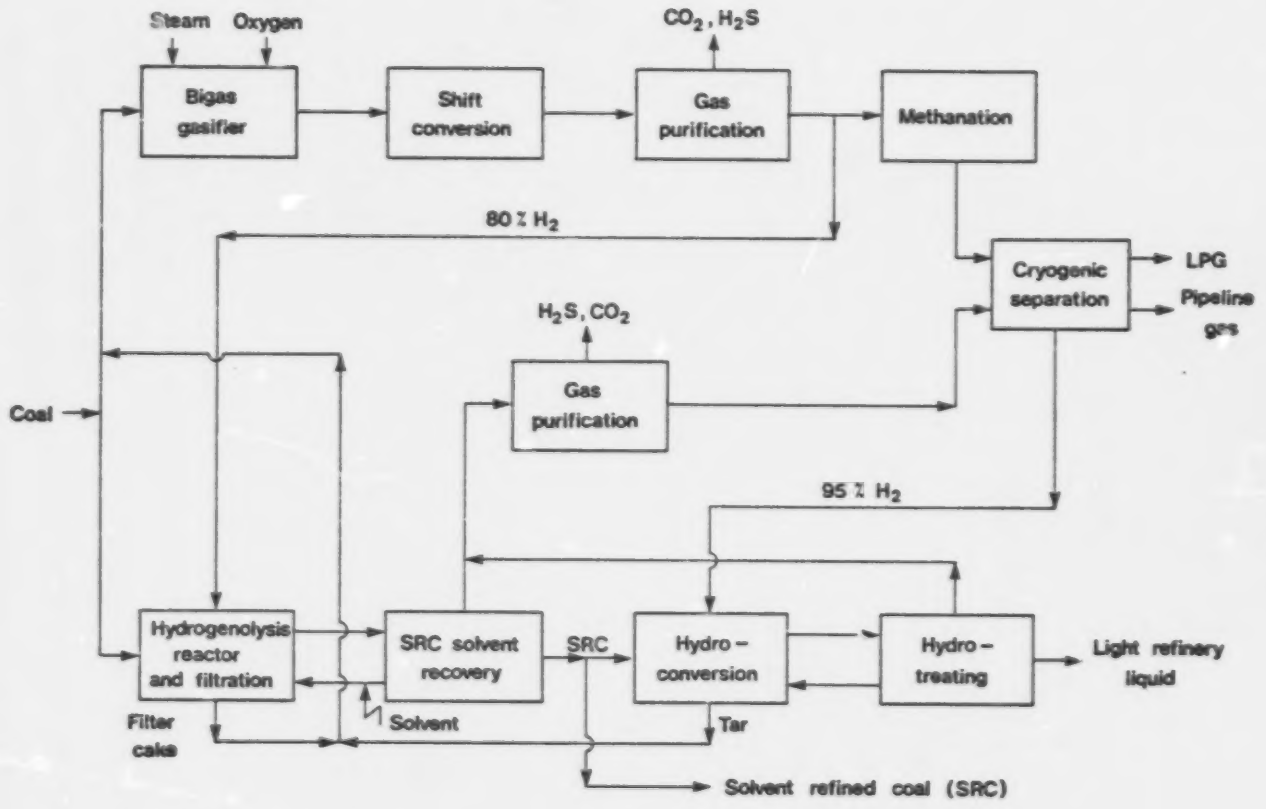
	Mg/day	Heat of Combustion TJ/day
Input		
Lignite for process	33,673	534.2
Lignite for steam and power	4,536	72.0
	38,209	606.2
Output		
Synthetic fuel oil	6,778	283.8
Hydrocarbon-rich fuel gas	1,985	95.5
Naphtha	1,752	79.8
Sulphur	210	2.7
Ammonia	248	5.7
	10,973	467.5

Overall thermal efficiency = $\frac{467.5}{606.2}$ X 100 = 77.1%

[1] from Baria (1975)

Figure 11

Simplified Flowsheet for COG Refinery



In the hydroconversion unit, the solvent refined coal is hydrogenolysed in the presence of a coal-derived solvent as in the H-Coal process. The solids and tar from this step are sent to the Bigas gasifier and the solvent is recovered and recycled. The liquid product is combined with light oil and sent to hydrotreatment to produce light refinery liquid. The off-gases from hydroconversion and hydrotreatment are sent to gas purification and the hydrogen and hydrocarbons recovered.

Coal (25 per cent of the total coal fed to the plant) and residue from the solvent refined coal and hydroconversion processes are converted in the Bigas reactor with oxygen and steam. The gases from the reactor are cooled, shifted and purified, a part is upgraded to pipeline quality substitute natural gas and the rest is used for hydrogen manufacture by cryogenic separation of methane and other hydrocarbons.

Major advantages include production of low cost fuels and an efficient use of coal energy. However, there may not be a market for all of the products obtained in a given locality where the COG plant is situated. As well, the inherent disadvantages of each process used will be present in the overall refinery.

A description of design criteria for a COG refinery is based on the commercial design by Chem Systems which used a bituminous Illinois coal (Baria, 1975). The design is for the production of 284 TJ per day of light refinery liquids and is based on the following assumptions:

a. lignite with its full moisture content is fed to the process;

b. the material and energy balances are calculated based on the ultimate carbon analysis;

c. seventy-eight per cent of the solvent refined lignite is used as fuel in the plant itself.

The material and energy balances for the COG refinery are shown in Table 26. The total lignite consumption is 43,389 Mg per day, and the main products are 6,232 Mg (7,450 kL) of light refinery liquids, 841 Mg (1,539 kL) of liquefied petroleum gas, 4.42 million standard cubic metres of pipeline

Table 26: Material and energy balance for the COG refinery[1]

	Mg/day	Heat of Combustion TJ/day
Input		
Lignite for solvent refined lignite	33,012	523.3
Lignite for Bigas	10,377	164.6
Oxygen for Bigas	3,290	-
Steam	5,977	-
	52,656	687.9
Output		
Light refinery liquid	6,232	283.8
Liquefied petroleum gas	841	43.0
Pipeline gas	3,256	175.0
Solvent refined lignite (for plant fuel)	3,760	136.9
Solvent refined lignite (product)	1,054	38.4
Sulphur	243	3.2
Ash	2,690	-
Phenols	66	2.4
Vent carbon dioxide	16,721	-
Water	16,141	-
	51,004	682.7

Thermal efficiency for process = $\frac{682.8}{687.9} \times 100 = 99.2\%$

Overall thermal efficiency = $\frac{682.8 - 136.9}{687.9} \times 100 = 79.4\%$

[1] from Baria (1975)

quality gas and 1,054 Mg of solvent-refined lignite per day. Another 3,760 Mg per day of solvent-refined lignite are consumed as fuel. The thermal efficiency for the process is 99.2 per cent and the overall thermal efficiency, taking into account the solvent-refined lignite used for fuel, is 79.4 per cent.

5.3.3. Donor Solvent Process

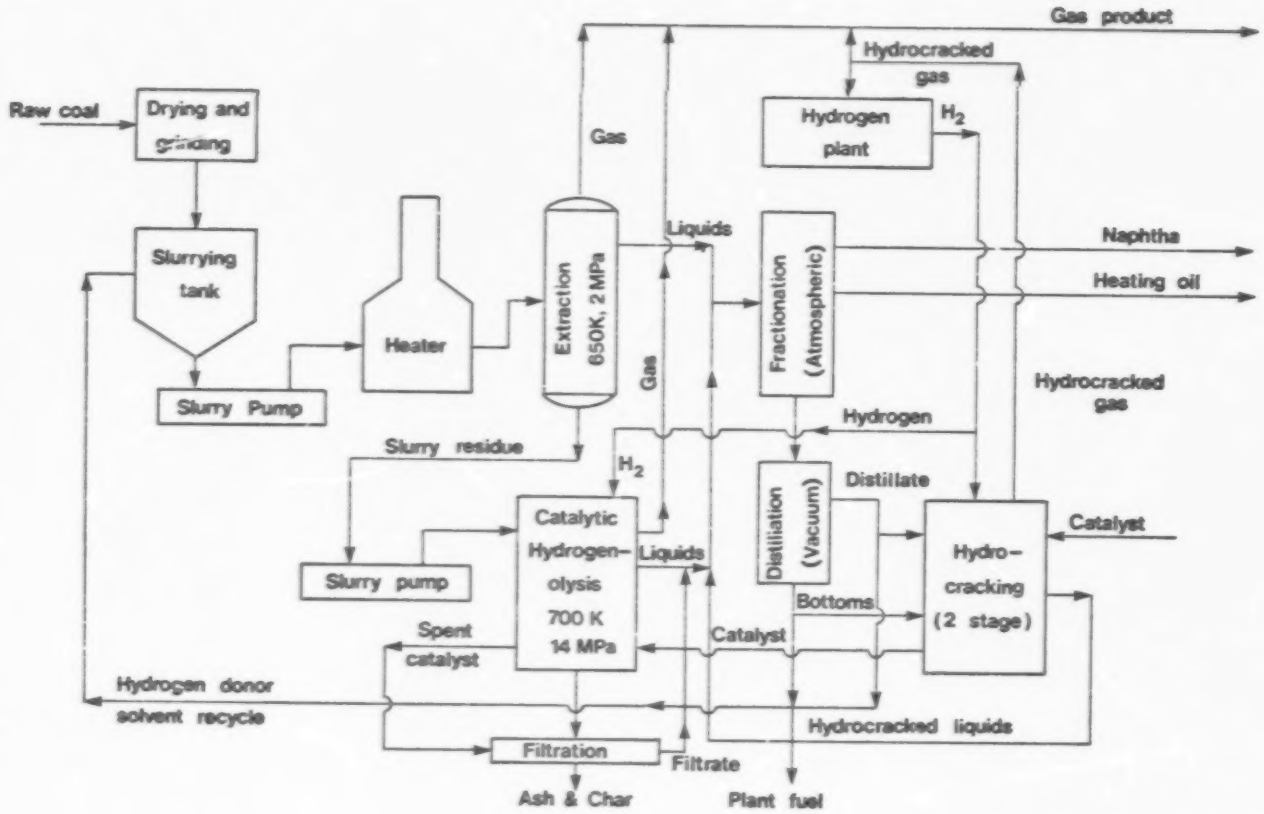
The preliminary development of this process was funded entirely by Exxon; however, ERDA began supporting operation of a small-scale unit in July 1976. Further development has continued at a 0.9 Mg/day pilot plant located in Baytown, Texas. The unit is providing data for process correlations and scaleups, as well as substantial quantities of product and bottoms for parallel research efforts. A 225 Mg/day pilot plant capable of processing 7,900 kL/day of a synthetic crude oil has recently been designed.

A simplified flowsheet of the Donor Solvent Process is shown in Figure 12(Furlong et al., 1976). The coal feed for the pilot plant is dried, ground, screened to -30 mesh and fed to the plant at a nominal rate of 50 kg/hour. Solvent-to-coal rates typically employed range from 1.1 to 2.0. The coal and recycle solvent are continuously metered into a slurry preparation vessel. A centrifugal pump used to circulate the slurry in this vessel maintains solids in suspension, as well as providing intimate contact between coal and solvent.

Three piston pumps move the slurry through the preheater and into the hydrogenolysis reactors. The combined, preheated streams of slurry feed and hydrogen flow through the reactors with a residence time of 15 to 240 minutes. Hydrogenolysis temperatures vary from 640 K to 750 K while the pressure is kept between 2 and 17 MPa. The hydrogen added varies from 0 to 17% (weight) of the coal feed. After gas separation, the slurried products flow to a vacuum tower for solids separation. The tower is operated at about 3.3 kPa and a flash zone temperature of about 640 K. Bottoms from this tower are removed at atmospheric pressure while the overhead product is separated in two streams, heavy vacuum gas oil, and light vacuum gas oil. The latter is combined with other liquid hydrocarbon streams from the hydrogenolysis reactor to produce feed for the solvent hydrotreating system.

Figure 12

Simplified Flowsheet for Donor Solvent Process



Fixed bed catalytic reactors usually containing cobalt-molybdate are used in the solvent hydrotreating system. Space velocity is typically between 0.5 and 2 hours^{-1}; temperature and pressure are in the range of 530 K to 720 K and 8 to 21 MPa respectively. The gas and liquid products from hydrotreating are separated and the liquid is sent to the solvent fractionation system. Solvent required for the hydrogenolysis reaction is recycled from this point to slurry preparation. The excess solvent is removed from the system as product. The off-gases from hydrotreatment units are sent to a gas purification system and the hydrogen and hydrocarbons are recovered.

A limited amount of information has been published on product quality and yields from the Donor Solvent Process. The process is directed toward production of naphtha blending components and low-sulphur fuel oil. In addition, various chemical components can be obtained as specialty products. Operation of pilot units have shown that, by adjusting the hydrogenolysis condition, the amount of naphtha produced can be varied from 5% (by weight) to at least 25% on a dry coal basis. Similar changes in oil quantity and boiling range can be achieved by varying hydrogenolysis conditions or by adjusting solvent properties.

Since the unconverted residue and depleted solvent are hydrogenated and hydrogenolyzed together, this approach should give higher conversions of coal to liquids, provided a cheap expendable catalyst is available.

5.4 Hydrogenolysis Under Pyrolytic Conditions

Hydrogenolysis processes under pyrolytic conditions (often called hydrocarbonization) are similar to low-temperature coal carbonization in that fluidized or entrained beds are used but pressurized hydrogen replaces air as the fluidizing medium. Many investigators have found that hydrogen tends to increase liquid yields, particularly as the partial pressure of hydrogen is increased. Several of these processes have been proposed as a more attractive route to liquid products than the high pressure Bergius hydrogenolysis process. Although liquid yields for hydrocarbonization are somewhat lower than for hydrogenolysis, the overall yields of gas plus liquids are comparable. Moreover, the difficult problems associated with pasting oil recycle and heavy oil letdown are avoided in hydrocarbonization. This category includes the Coalcon and the Clean Coke processes.

5.4.1 Coalcon

Although few details have been released, the Coalcon process appears to combine pyrolysis and uncatalyzed hydrogenolysis to produce 240 L of oil and 22 standard cubic metres of pipeline gas per Mg of coal (Morgan, 1976).

For this process the feed coal is crushed, ground and dried in contact with hot flue gas so that 50% of the material passes through 100 mesh, and moisture is reduced to 1%. The coal is then heated (also with hot flue gases from the plant utility boiler) before being fed to the reactor from pressurized lock hoppers using hydrogen as a carrier.

Hydrogen produced by char gasification is mixed with recycle from the hydrogen purification step, and then preheated and fed into the reactor. The hydrogenolysis reaction occurs at moderate conditions, 830 K and 3.8 MPa. Hydrocarbon vapours and gas from the reactor overhead are quenched, cooled, and fractionated to yield a light and a heavy fuel oil product. The char is removed from the bottom of the reactor and gasified to produce make-up hydrogen. Excess char or gasified residue is employed as fuel for steam generation.

The non-condensed vapours in the process gas from the reactor are treated to remove NH_3, CO_2 and H_2S. The scrubbed gas is sent to hydrogen purification by cryogenic methods.

A demonstration plant with a nominal capacity of 2,540 Mg/day coal is being designed and is scheduled for completion in 1979. It is expected to produce 620 kL/day of low-sulphur fuel oil and the equivalent of 620×10^3 standard cubic meters per day of pipeline gas. The project is sponsored jointly by the Coalcon group and the U.S. Government under the "Clean Boiler Fuel from Coal" program.

5.4.2 Clean Coke

A method developed recently for the purpose of producing coke from high-sulphur bituminous coals is U.S. Steel's "Clean Coke" process, a combination of low-temperature carbonization and solvent-phase hydrogenolysis (Ferretti, 1976).

The coal, after beneficiation and sizing in a coal preparation plant, appears as two fractions, a low-sulphur, low ash fraction with most of the inorganic sulphur removed and a high-sulphur, high-ash fraction. The former is fluidized by a hydrogen-rich stream of recycle gas in the carbonizer, pyrolyzed at temperatures up to 1,014 K and pressures to 1.14 MPa to produce gas, tar, and char, which serve as base materials for the production of metallugical coke. Gases evolved during carbonization are cooled to condense tars and oils, scrubbed in an acid gas absorber, heated, and then recycled to provide heat in the carbonizer.

One advantage of this system is that desulphurization takes place during carbonization. As well, the process produces a net make of hydrogen which can be used for tar hydrotreating.

book

CHAPTER 2

EXPERIMENTAL HYDROGENOLYSIS OF A SASKATCHEWAN LIGNITE

1.0 PROCEDURES

1.1 Pre-Treatment and Analysis of Lignite

Approximately 75 kg of lignite were collected from Manalta Coal Limited's Klimax mine in Estevan, Saskatchewan. The air in the containers was flushed out with carbon dioxide, and the lignite was sealed from the atmosphere and shipped to Sherbrooke, Quebec.

Approximately 15 kg of sample were wasted to develop a standard grinding procedure. A description of the method is given as follows.

A second 15 kg of lignite were placed in a hermetically sealed fume hood, continually flushed with nitrogen. The samples were hand crushed with a porcelain mortar until the particles were less than 1 cm diameter. Five hundred gram samples of crushed lignite were pulverized in a porcelain ball mill flushed with nitrogen until approximately 75% of the material was -200 mesh (Tyler screen size), and the product was stored in sealed containers.

The fines content of the pulverized lignite was determined by a standard wash test described as follows. Firstly, the moisture content of the material was determined by drying to constant weight in a 380 K oven. A ten gram sample was placed on a U.S. no. 200 screen and wetted for a few seconds with a gentle water spray. The sediment was then washed at a constant water pressure and flow for 120 seconds. The fines were then filtered and dried to constant weight.

Samples of ground lignite were analysed for elemental carbon, oxygen, nitrogen, hydrogen and sulphur, and for moisture, ash, humic acid, fulvic acid, humins, fixed carbon and volatile matter content. To gain insight into the catalytic activity of the feed, the lignite was also analyzed for the following metals: aluminium, cobalt, copper, iron, potassium, lithium, manganese, molybdenum, sodium, nickel, tin and vanadium.

The elemental composition of lignite was determined instrumentally, using a Perkin-Elmer Model 240 Elemental Analyzer. Analysis was conducted on moisture free, 1 to 5 mg samples.

Moisture content was determined by two different methods: oven drying and xylol distillation. The first consisted in drying a 5 g sample of pulverized lignite to constant weight in an oven at 380 K.

For the xylol distillation, a sample of pulverized lignite was added to a distillation flask connected to a condenser and a calibrated distilling receiver tube. Just enough xylol was added to cover the sample. The mixture was distilled until nearly all the water was carried over into the receiver tube, as evidenced by a clearing of the xylol fraction. The condenser was rinsed with xylol and swabbed down with a neoprene rubber washer. Distillation and swabbing were continued until there was a lack of water droplets in the condenser. The time required for a distillation was two to three hours. The water content was read directly from the calibrated receiver tube.

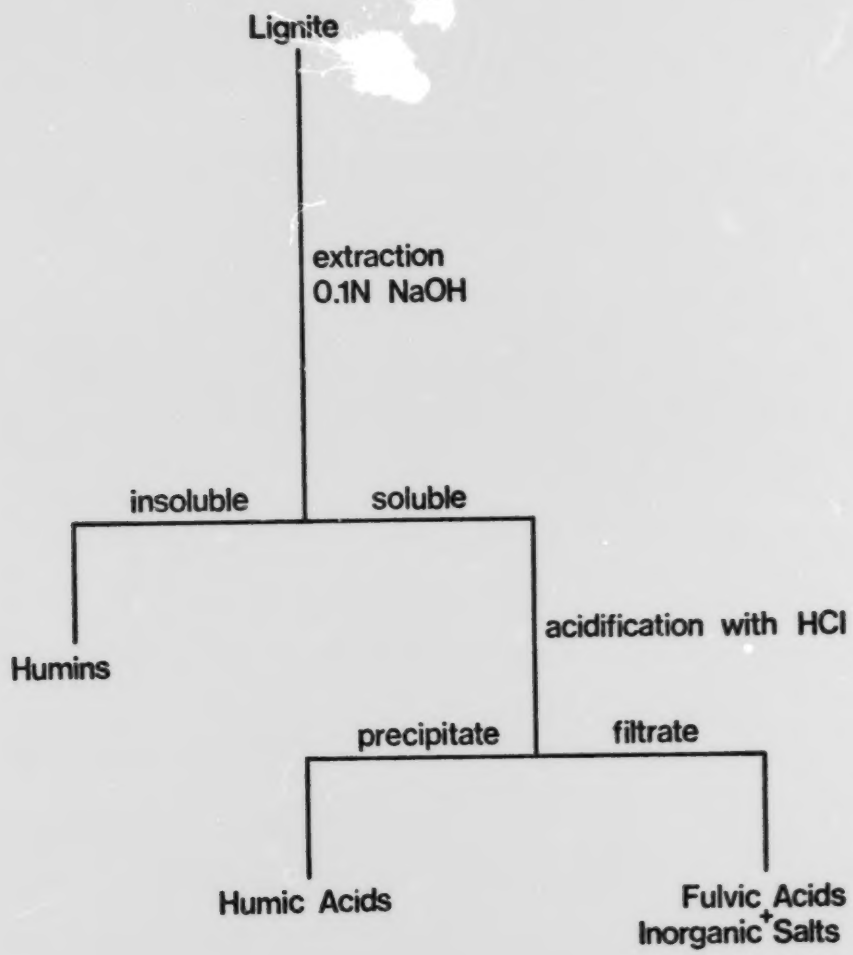
Ash content was determined by volatilizing a lignite sample with air in an oven to constant weight. The ashing was conducted at three temperatures: 710 K, 820 K and 1,020 K.

The volatile matter was taken as the loss in weight obtained by heating moisture free lignite for seven minutes in a covered crucible at 1,220 K. Fixed carbon was calculated as total weight of lignite as received minus the sum of moisture, ash and volatile matter.

A flowchart for determination of humic substances is presented as Figure 13. A mixture of 0.1 N sodium hydroxide (NaOH) solution and lignite in the ratio 10 L NaOH solution/100 g dry lignite was agitated at room temperature for 24 hours. Fulvic acids and humic acids dissolved in the base leaving the humins as a solid residue. The mixture was left undisturbed for another 24 hours to allow the solids to settle. After decantation of the clear solution, the suspended solids were centrifuged at 2,000 G for 5 minutes. The supernatant was saved and the residue was washed with 0.1 N NaOH. Centrifugation and washing were repeated twice, each time saving the supernatant. The residue was washed with distilled water, dried to constant weight and reported as humins content. The first decanted solution was combined with the supernatant and washings. The combined solution was acidified with 3 N hydrochloric acid to a pH of 2. The humic acids precipitated out of solution while fulvic acids remained in solution. The mixture was left undisturbed for 24 hours to allow the precipitate to settle. The clear supernatant was decanted from the mixture and discarded. The precipitate was centrifuged at 2,400 G for 10 minutes and the resulting supernatant discarded. The residue was repeatedly washed and centrifuged twice, discarding the washings after each step. The wet solid was dried in an oven at 340 K to constant weight, and reported as humic acids content. The weight of fulvic acids was calculated by difference.

Figure 13

Flow Chart for the Determination of Humic Substances



Metal analyses were conducted by ashing a 5 g sample of lignite (as received), dissolving the ash and determining metal content instrumentally. Two ashing techniques were employed, dry ashing and wet ashing.

Lignite was dry ashed by heating in an oven with air at 1120 K. The residue was leached with several portions of warm aqua regia to dissolve the metals. The solution was then diluted to 50 mL with distilled water.

The wet ash technique consisted in digesting a 5 g sample of lignite in a 4/30/1 volumetric mixture of concentrated perchloric/nitric/sulphuric acids. The mixture was gently heated in a sand bath to approximately 490 K until all the carbon was oxidized, which was evidenced by the mixture clearing. The solution was then cooled and diluted to 50 mL with distilled water.

Each solution of metals was analyzed for lithium and vanadium by flame emission spectroscopy and for other metals by atomic absorption spectroscopy.

1.2 Hydrogenolysis Experiments

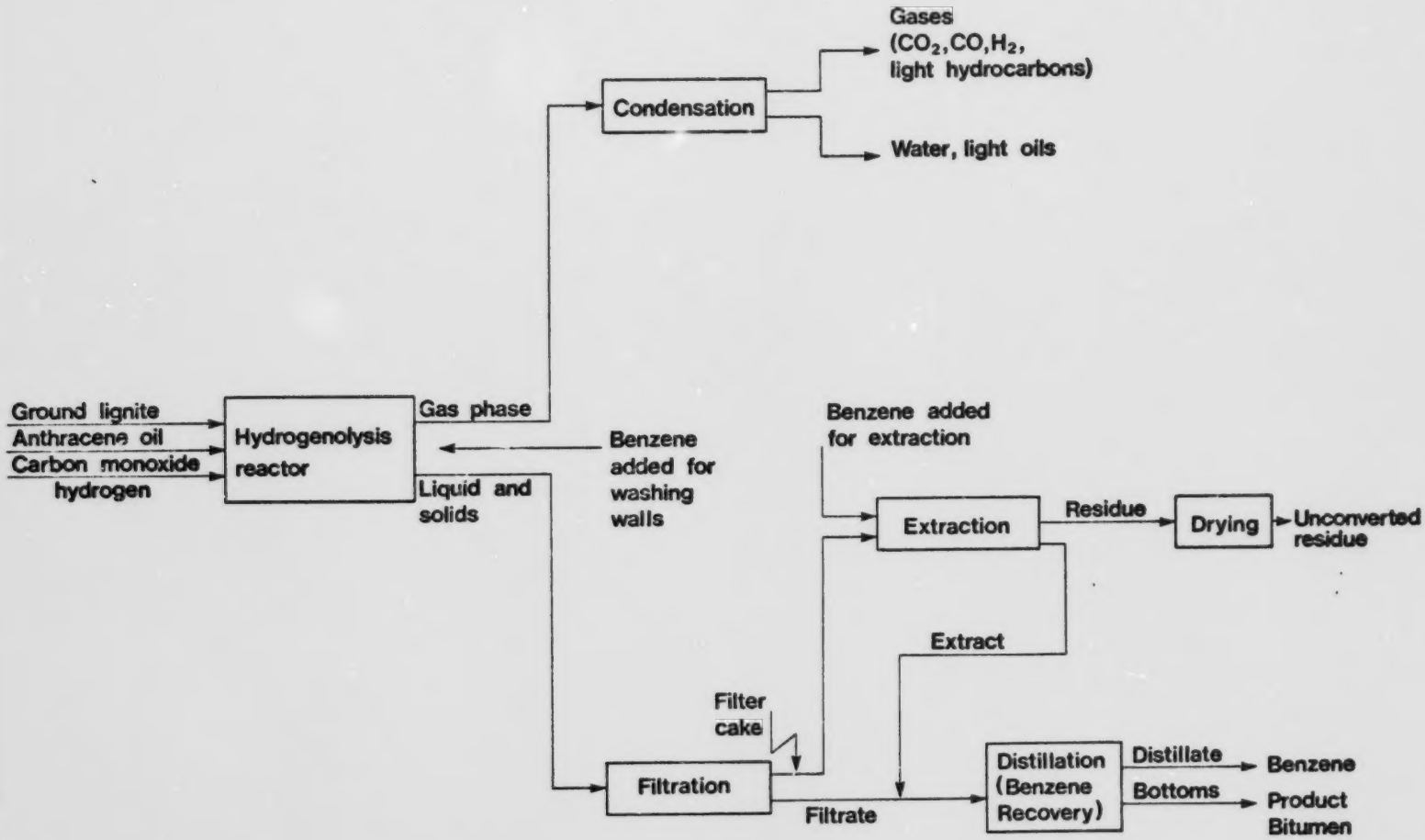
A flowsheet summarizing the steps involved with the hydrogenolysis experiments is presented as Figure 14. A known quantity of pulverized lignite was combined with anthracene oil at a solvent/feed mass ratio of 2.8/1. The mixture was sealed in a 1 litre Parr autoclave constructed of Inconel 600 alloy, and placed in a heating jacket attached to a rocker mechanism. The reactor was equipped with a thermocouple well for monitoring temperature and a pressure guage, and was connected to variable leak valves for gas introduction and sampling by 3.2 mm outside diameter stainless steel tubing.

The contents of the autoclave were flushed with hydrogen until essentially no oxygen or nitrogen could be detected by a gas chromatograph. Carbon monoxide and more hydrogen were introduced into the reactor to a specified pressure and composition. The initial gas composition was determined by chromatographic analysis.

The autoclave was heated at a controlled rate with agitation (rocking) to the reaction temperature. Gas composition was monitored during the heating phase for a selected number of experiments. The mixture was kept at the specified temperature and agitated for a known reaction time. Gas composition was determined periodically throughout the reaction by chromatography.

Figure 14

Flowsheet for Hydrogenolysis Experiments



At the end of the reaction, the mixture was quenched by removing the autoclave from the heating mantle and cooling by blowing air over the reactor. When the temperature was reduced to 380 K, the reactor was placed in the heating mantle and kept at this temperature during gas recovery.

A schematic diagram of the gas recovery procedure is presented in Figure 15. The vapours were vented through a series of coils and condensers to recover water and light oils. The total gas volume vented was measured by a wet test meter and the final composition was determined with a gas chromatograph.

The condensed liquid in the trap immersed in ice water was recovered, weighed and stored in a sealed jar. This product consisted mainly of water and some light oils.

The condensed material in the trap immersed in liquid nitrogen was vapourized at room temperature. The gas composition was monitored to detect the presence of light hydrocarbons, and the volume measured by a wet test meter.

Immediately after venting the gases from the autoclave, the reactor was removed from the heating jacket and placed on a revolving support. The reactor head was removed and the condensed phase processed for recovery. A schematic diagram of the liquid recovery procedure is given as Figure 16. The liquid and solid products were poured through a pre-weighed Whatman Number 5 filter placed on a pre-heated (to 380 K) porcelain Bückner funnel. To facilitate filtration, the receiving flask was kept under a moderate vacuum (approximately 20 kPa) and the filtering apparatus externally heated to maintain a temperature of 330 K. The autoclave interior was thoroughly washed with benzene and the washings filtered with the products.

The filter cake, containing solid residue, non-filterable bitumen and adsorbed oils, was extracted with benzene for approximately 72 hours in a soxhlet apparatus, until no colouration was observed in the liquid extract. The residue, containing unextracted or unconverted components, was dried in an oven at 380 K for approximately 14 hours, weighed and stored in a dessicator.

The liquid extract was combined with the filtrate from the autoclave, and the mixture distilled in a rotary flash evaporator at 305 K and 20 kPa to recover benzene. The bottoms, containing oils, tars and anthracene oil, were weighed, sealed in a jar and stored for chemical analysis.

Figure 15

Schematic of Gas Sampling and Recovery Procedure

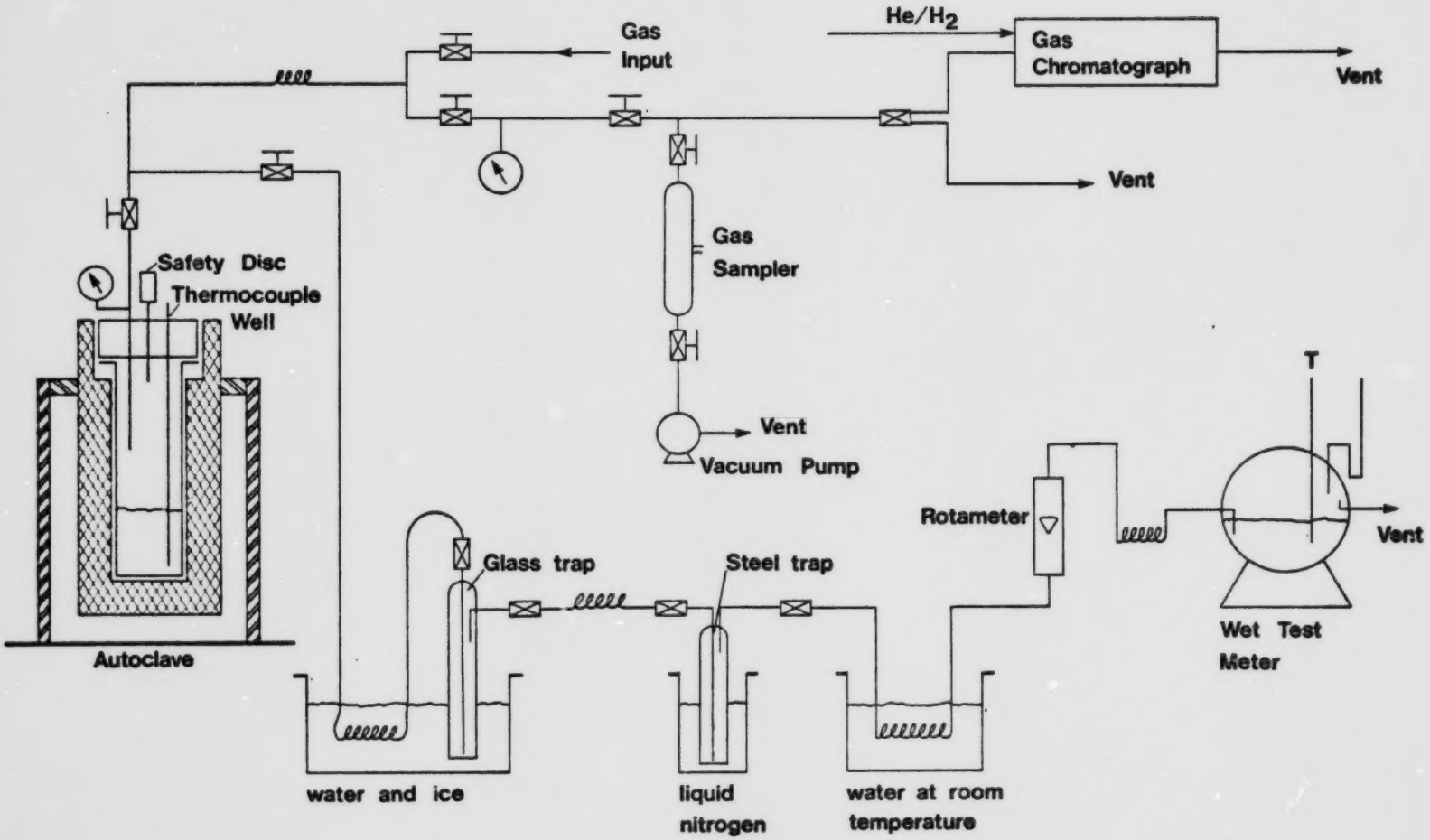
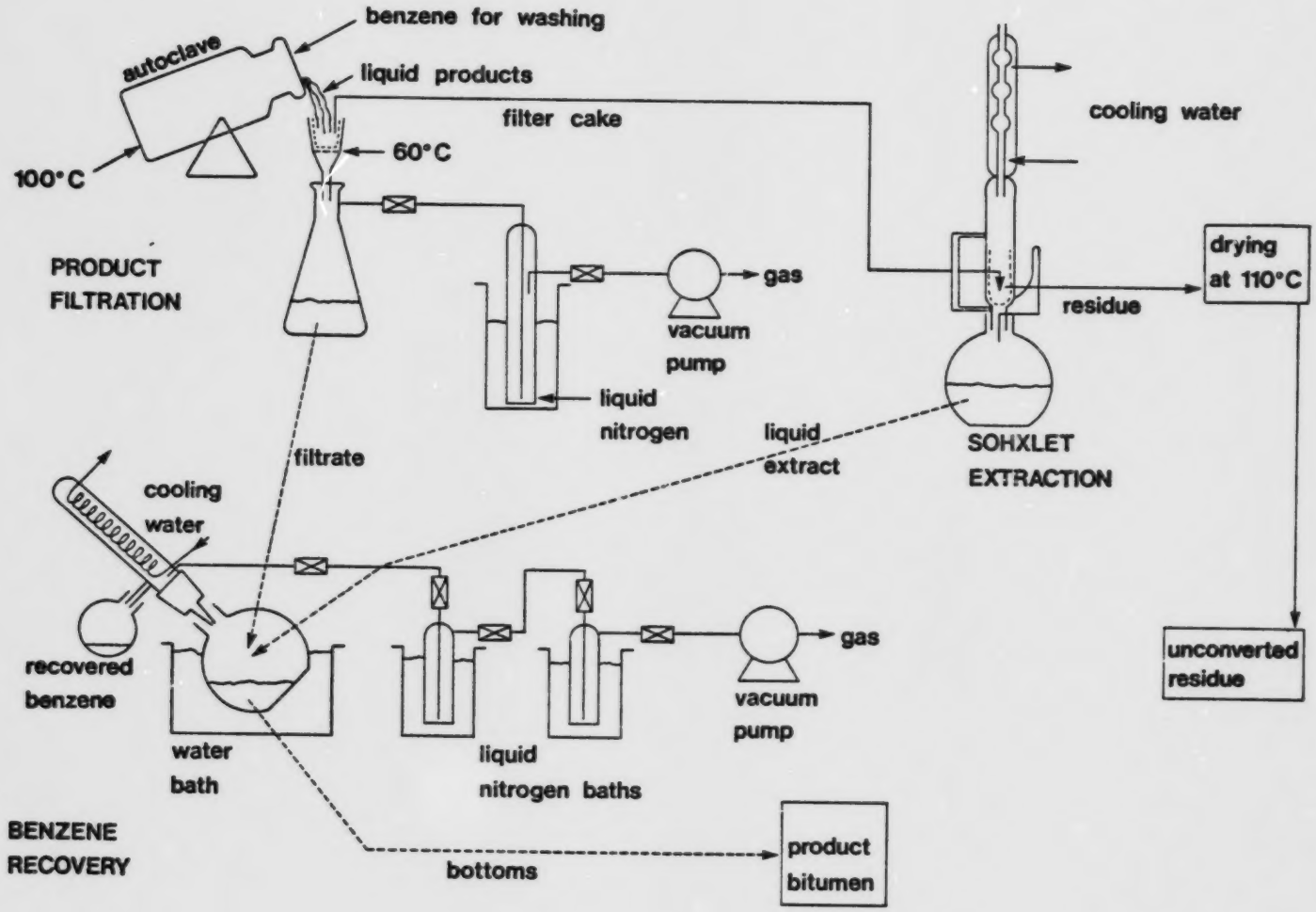


Figure 16

Schematic of Liquid Recovery Procedure



Conversion was calculated using the following formula:

$$\text{Conversion (weight \%)} = 100 - \frac{100\ (R-LTA)}{L} \qquad (1)$$

where R is the weight of unconverted and unextracted residue

LTA is the weight of ash in the moisture free lignite feed (determined by the low temperature ashing method at 710 K)

L is the weight of moisture and ash free lignite charged to the reactor

The liquid oil yield was calculated with the following formula:

$$\text{Liquid oil yield (weight \%)} = \frac{100\ (F+E-AO)}{L} \qquad (2)$$

where F is the weight of benzene free filtrate

E is the weight of benzene free extract

AO is the weight of anthracene oil charged to the reactor

L is the weight of moisture and ash free lignite charged to the reactor

Both of the above parameters are conservative estimates of the true conversion and oil yield. When calculating conversion, it was assumed that residues left in the autoclave after washing and left on the filter paper after removing the filter cake were unconverted components. When calculating oil yield, the light oils condensing with water in the ice water trap were not considered.

1.3 Analysis of Gas Phase

During the course of the experiment, the gas phase was periodically analyzed by a Perkin-Elmer Model 3920 gas chromatograph where a system of two columns separated the different products.

A known volume (usually 0.4 - 0.5 cm^3) of reaction gases which had previously been collected in a 500 mL sampler was injected into the hydrogen/helium carrier flowing at 20 mL/min. The mixture passed through a 1.83 m length, 3.2 mm outside diameter column packed with 80/100 mesh Porapaq Q and a 1.37 m length, 3.2 mm outside diameter column packed with 80/100 mesh molecular sieve 5A. The columns were isothermally maintained at 343 K.

Hydrogen (H_2) was detected within one minute after injection. Immediately after H_2 passed through, the Porapaq Q column was isolated by manipulation of the switching valve. In this way, the mixture was carried only through the other column which isolated oxygen, nitrogen, methane and carbon monoxide in that order. After carbon monoxide was detected, the switching valve was again manipulated to allow the mixture to pass through the Porapaq Q column. This column isolated carbon dioxide, ammonia, ethylene, ethane and water in that order.

In order to detect a higher molecular weight hydrocarbons, the column temperatures were increased up to 423 K.

For each gas present in the mixture, the chromatograph detector produced a curve on the recorder. The composition of the mixture was determined by comparing the area under the curves with other peaks produced by a gas of known composition.

1.4 Analysis of Liquid Phase

The elemental composition of the product oil was determined instrumentally, using a Perkin-Elmer Model 240 Elemental Analyzer.

The viscosity of the oils was determined using an Oswald-Cannon-Fenske capillary tube viscometer at 333 K.

1.5 Experimental Design

1.5.1 No Catalyst Addition

Two sets of experiments were conducted: one where no catalyst was added to the reaction mixture, and the other where catalysts were employed to decrease the oxygen content of the liquid oil products.

The first set of experiments (no catalyst added) were conducted according to an unreplicated 2^4 factorial design. In this case, two values (levels) of four experimental variables (factors) were considered to study their effects on various results (response variables).

A summary description of the experimental design is given in Table 27. The factors studied were reaction temperature, initial gas composition, initial pressure and residence time. Both a low and a high level were considered for each factor. Therefore, the number of experiments required for the design was 16 ($=2^4$). Three responses were considered: conversion, liquid oil yield and oxygen content of the liquid oil.

Normally, each experiment (treatment) is repeated to provide a measure of the experimental error. However, to minimize the number of tests conducted, the design was unreplicated, and the error was estimated from three treatments conducted at the following mid-point level:

reaction temperature	:	693 K
carbon monoxide/hydrogen molar ratio	:	1/1
initial pressure at room temperature	:	9.1 MPa
residence time at reaction temperature	:	30 minutes

The design matrix (array of treatments) written in a standard order named "Yates' order" is given in Table 28. The factors are labelled A, B, C and D; the high level of each variable is indicated by the presence of the associated lower-case letter and the low level by the absence of a letter. The symbol 1 represents the treatment in which all factors appear at their low level.

The design matrix written in a second notation is given in Table 29. The factors are labelled X_1, X_2, X_3 and X_4; the high level of each variable is indicated by +1, the low level by -1, and the central level by 0.

1.5.2 Catalytic Screening

Eight screening experiments were conducted to lower the oxygen content in the liquid oil product by catalytic methods. The experimental conditions were at the mid-point level described in the previous section above.

Table 27: Summary of experimental design for experiments without added catalysts

Experimental Variables	Levels	
	Low	High
1. Reaction temperature (K)	653	733
2. Carbon monoxide/hydrogen molar ratio	0.33/1	3/1
3. Initial pressure (MPa)	7.1	11.1
4. Residence time at reaction temperature (min)	10	50
Response Variables		
1. Conversion		
2. Liquid oil yield		
3. Oxygen content of liquid oil		

Number of experiments 2^4 = 16

Number of replicates at central point = 3

Total number of experiments = 19

Table 28: Design matrix for experiments without added catalysts - first notation

Experiment Number	Treatments
1	1
2	a
3	b
4	ab
5	c
6	ac
7	bc
8	abc
9	d
10	ad
11	bd
12	abd
13	cd
14	acd
15	bcd
16	abcd

A: reaction temperature
B: initial gas composition
C: initial pressure at room temperature
D: residence time at reaction temperature

Table 29: Design matrix for experiments without added catalysts - second notation

Experiment Number	Treatments			
	X_1	X_2	X_3	X_4
1	-1	-1	-1	-1
2	+1	-1	-1	-1
3	-1	+1	-1	-1
4	+1	+1	-1	-1
5	-1	-1	+1	-1
6	+1	-1	+1	-1
7	-1	+1	+1	-1
8	+1	+1	+1	-1
9	-1	-1	-1	+1
10	+1	-1	-1	+1
11	-1	+1	-1	+1
12	+1	+1	-1	+1
13	-1	-1	+1	+1
14	+1	-1	+1	+1
15	-1	+1	+1	+1
16	+1	+1	+1	+1
Central level	0	0	0	0

X_1 : reaction temperature
X_2 : initial gas composition
X_3 : initial pressure at room temperature
X_4 : residence time at reaction temperature

Two process methods were tested:

- adding a catalyst in the reactor and conducting conversion and deoxygenation simultaneously.

- conducting the conversion in the primary reactor followed by oxygen removal in a separate reactor after solids separation.

The catalysts used were cobalt molybdate on alumina containing various concentrations of potassium promoter. These were supplied by Energy, Mines and Resources Canada.

2.0 RESULTS AND DISCUSSION

2.1 Feedstock Characteristics

The results of the ultimate and proximate analysis of the lignite and anthracene oil (Crowley tar) are given in Table 30. The anthracene oil consisted principally of hydrocarbons, containing less than 5% heteroatoms. No moisture or ash was detected. The lignite had low sulphur (0.5% mf) and nitrogen (1.2% mf) contents but high moisture (34.4%) and oxygen (22.2% mf).

Table 31 presents the results of "active metal" analyses on three lignite samples. Both wet and dry ash analysis produced similar results except in the case of iron (Fe) where dry ashing recovered only 35% of Fe found with the alternate method. The results show that 98% of the active metal fraction in lignite consists of Na, Al and Fe. The presence of all the metals explains the catalytic activity of the ash fraction.

2.2 Experiments Without Added Catalysts

2.2.1 Experimental Conditions

Table 32 presents the experimental parameters and their values which were varied during the experimental programme. The reaction temperature was changed from 653 to 733 K at 40 K intervals, the initial pressure at room temperature from 7.1 to 11.1 MPa at 2.0 MPa intervals, the CO/H_2 ratio from 0.33/1 to 3/1 or the mole fraction of CO from 0.25 to 0.75 at 0.25 intervals, and the residence time at a reaction temperature from 10 to 50 minutes at 20 minute intervals. The parameters kept constant for all experiments and their value are given in Table 33. No catalyst was added and anthracene oil was used as solvent. The moisture and ash added to the reactor were naturally occurring in the lignite.

Typical temperature and pressure profiles measured during the heating, cooling and reaction periods are given in figures 17 to 20. The figures show that approximately 30 minutes were required for the reaction temperature to stabilize, but heating and cooling rates were fairly constant. The reaction temperature was reached after 45 to 50 minutes of heating and the reactor cooled to less than 400 K after approximately one hour. The shape of the pressure and temperature profiles were nearly identical to each other.

Table 30: Feedstock Characteristics[1]

Anthracene Oil

Ultimate Analysis[1]:

carbon	:	89.4
hydrogen	:	5.9
oxygen	:	1.8
sulphur	:	0.5
nitrogen	:	0.7

Lignite

Ultimate Analysis[2]:

carbon	:	60.4
hydrogen	:	3.6
oxygen	:	22.2
sulphur	:	0.5
nitrogen	:	1.2
ash	:	14.2

Proximate Analysis[1]:

moisture	:	34.4
ash	:	9.3
fixed carbon	:	29.1
volatile matter	:	27.2
humic acids	:	17.3
fulvic acids	:	2.4
humins	:	36.6

[1] basis: per cent by weight as received

[2] basis: per cent by weight moisture free

Table 31: Results[1] of the analysis of lignite for metals

Metal	Sample #1		Sample #2		Sample #3	
	Wet Ash [2]	Dry Ash [3]	Wet Ash	Dry Ash	Wet Ash	Dry Ash
Al	5690	5990	6350	6190	5530	5950
Co	1.8	1.7	2.2	1.6	2.2	1.7
Cu	4.2	3.9	4.1	4.2	4.3	4.0
Fe	2560	940	2730	920	2760	930
K	141	129	152	146	140	144
Li	0.62	0.50	0.63	0.56	0.68	0.51
Mn	25.1	22.1	25.5	22.1	25.3	22.0
Mo	3.2	2.0	3.2	1.9	2.8	2.0
Na	6760	5140	5840	6460	5800	6030
Ni	3.7	2.4	4.3	3.3	3.6	3.3
Sn	3	4	4	4	3	3
V	26	31	26	35	28	28

1 expressed as µg metal/g lignite as received

2 involves acid digestion of lignite at room temperature

3 involves ashing lignite at 1120 K

Table 32: Experimental conditions for treatments without added catalysts

Experiment Number	Treatments	Reaction Temperature K	Initial Pressure At Room Temperature MPa	Initial Gas Composition CO/H_2 molar ratio	Residence Time At Reaction Temperature min
1	1	653	7.1	0.33/1	10
2	a	733	7.1	0.33/1	10
3	b	653	7.1	3/1	10
4	ab	733	7.1	3/1	10
5	c	653	11.1	0.33/1	10
6	ac	733	11.1	0.33/1	10
7	bc	653	11.1	3/1	10
8	abc	733	11.1	3/1	10
9	d	653	7.1	0.33/1	50
10	ad	733	7.1	0.33/1	50
11	bd	653	7.1	3/1	50
12	abd	733	7.1	3/1	50
13	cd	653	11.1	0.33/1	50
14	acd	733	11.1	0.33/1	50
15	bcd	653	11.1	3/1	50
16	abcd	733	11.1	3/1	50
17	central level	693	9.1	1/1	30
18	central level	693	9.1	1/1	30
19	central level	693	9.1	1/1	30

Table 33: Parameters fixed for all experiments

Parameter	Value
catalyst/feed ratio (maf lignite)	0/1
solvent/feed ratio (maf lignite)	2.8/1
moisture (maf lignite)	59%
ash (maf lignite)	18%
lignite particle size	75% at - 200 mesh
heating rate of reactor	-
cooling rate of reactor	-

Figure 17

Temperature and Pressure Profiles - Experiment 1

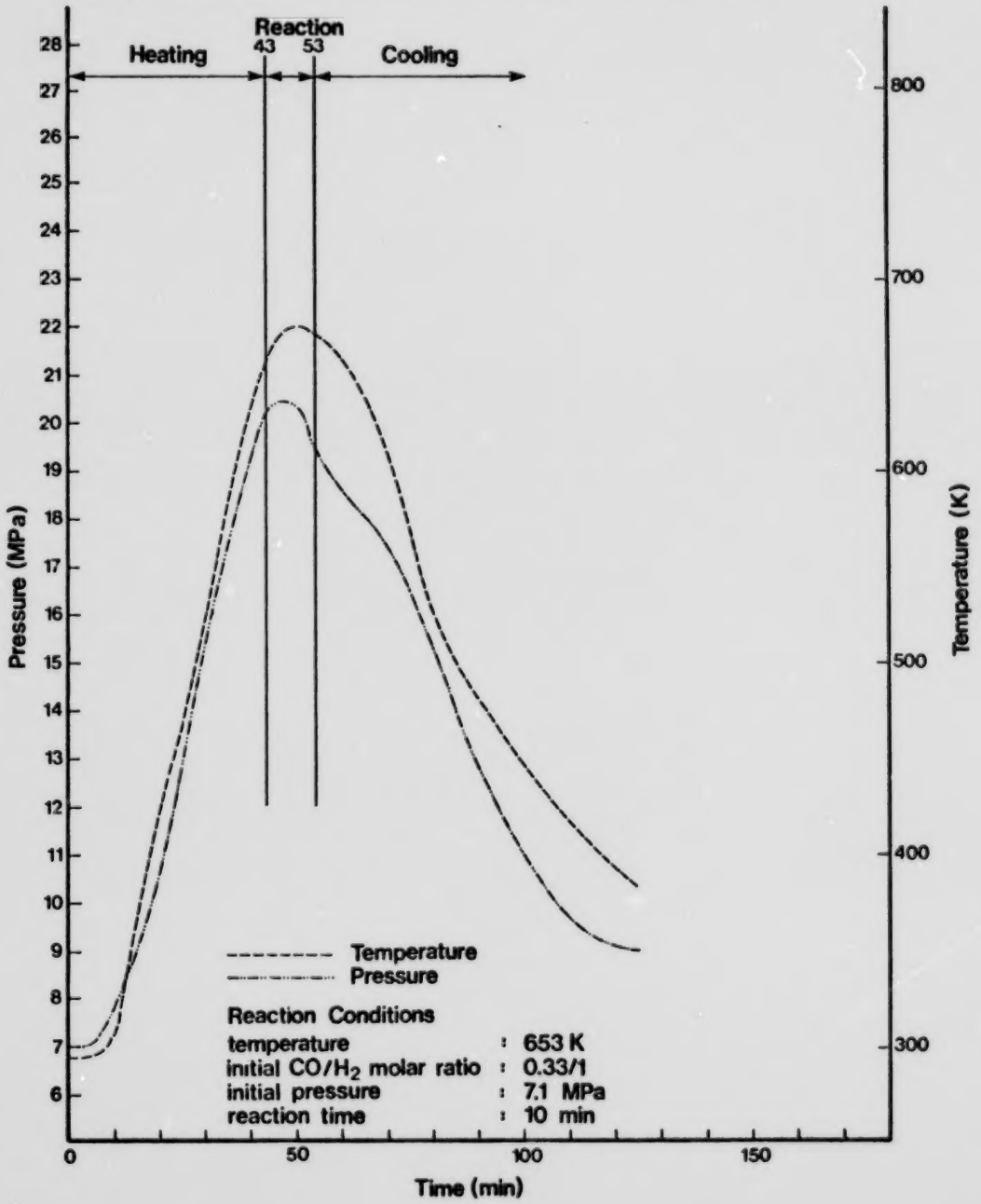


Figure 18

Temperature and Pressure Profiles - Experiment 10

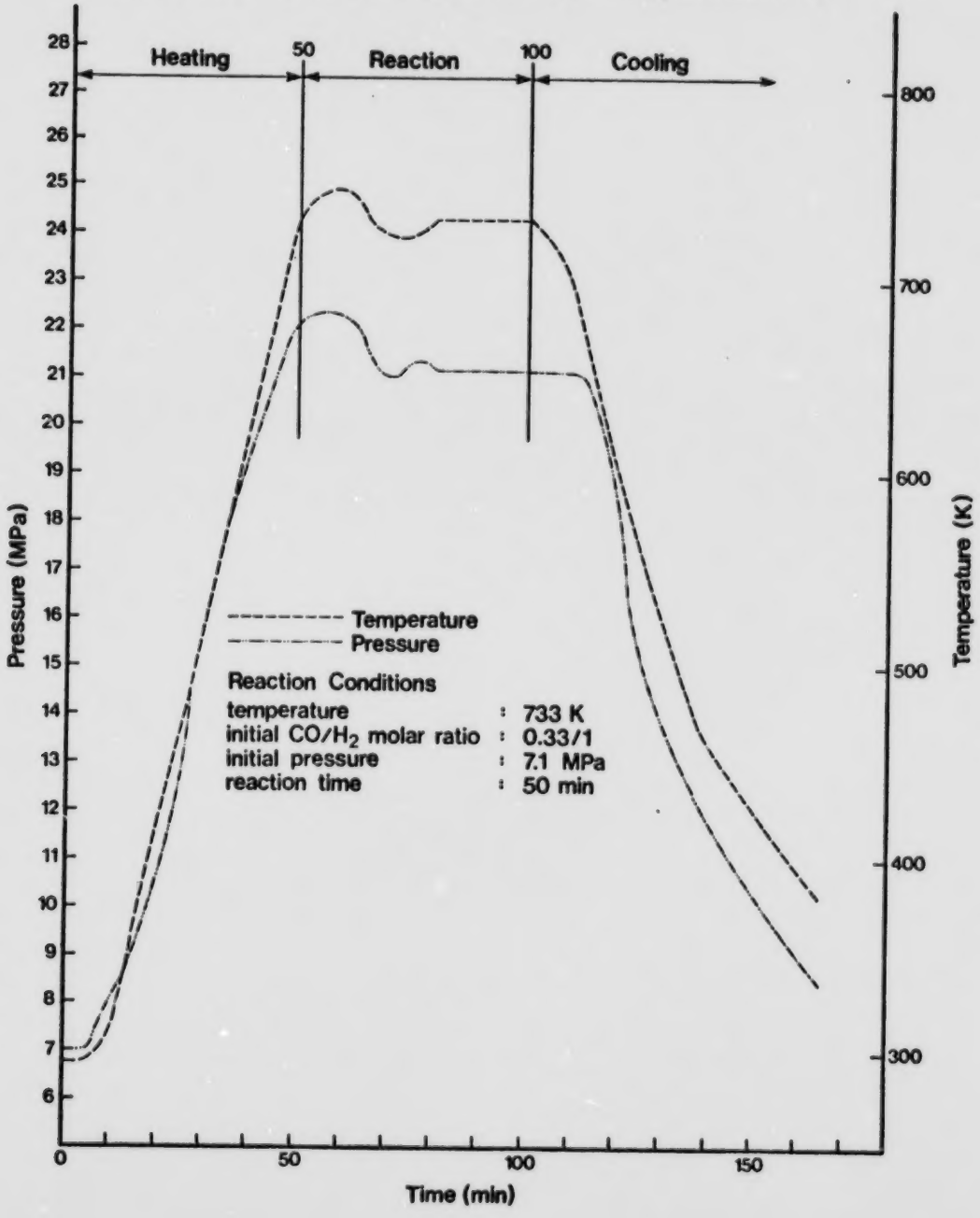


Figure 19

Temperature and Pressure Profiles - Experiment 11

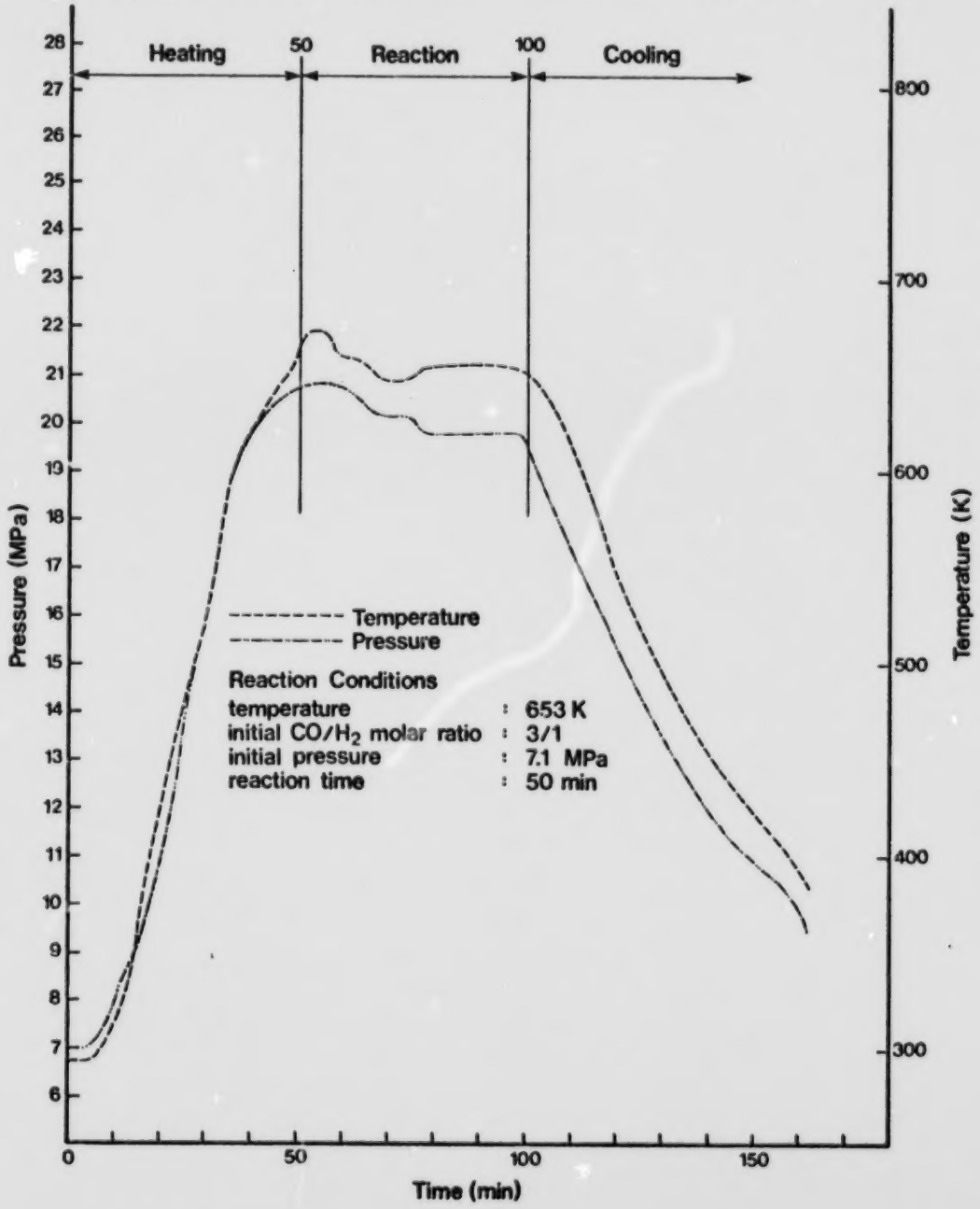
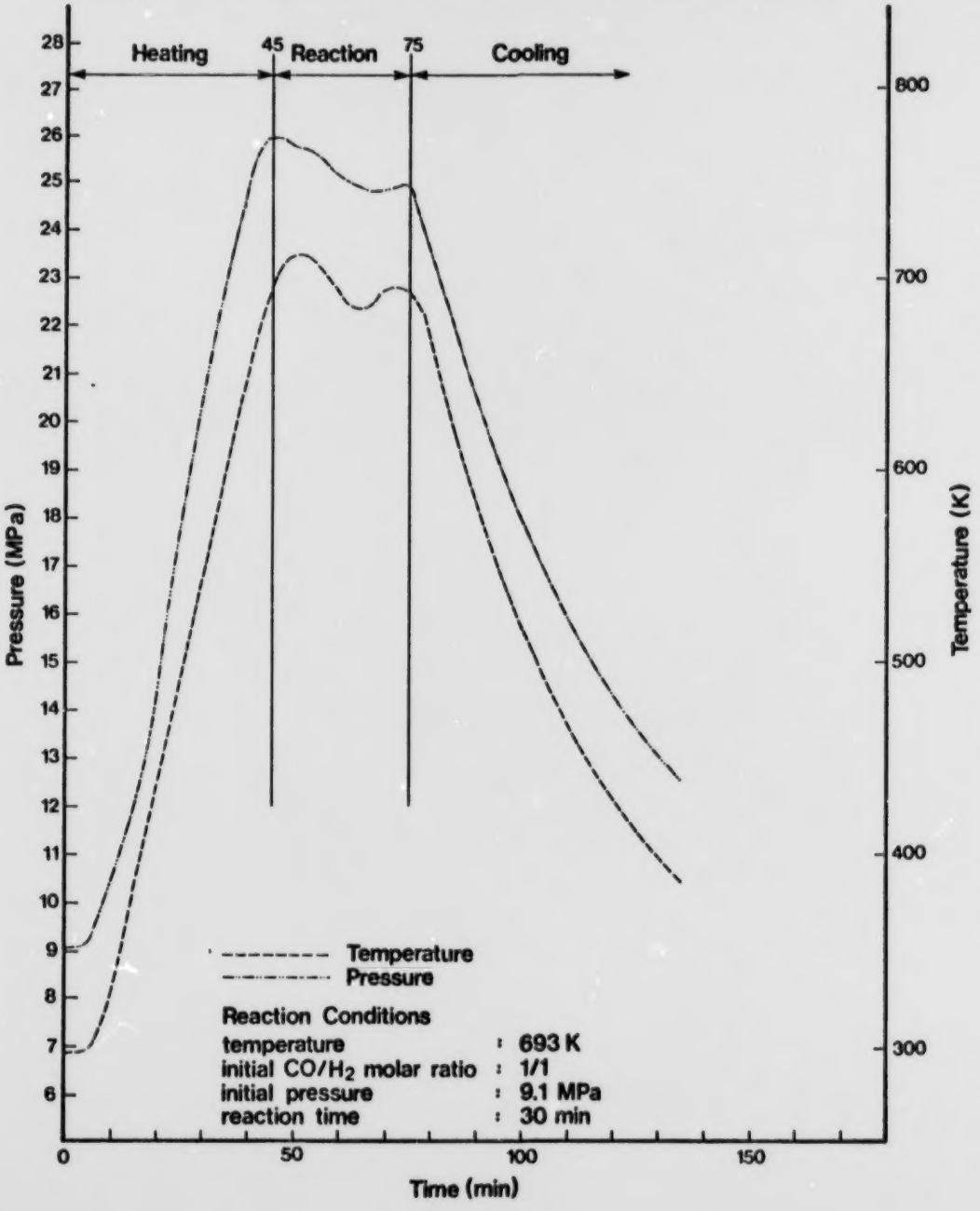


Figure 20

Temperature and Pressure Profiles - Experiment 17



2.2.2 Feedstock and Products

Table 34 presents the weight of each component fed into the reactor for hydrogenolysis. The weight of products obtained from each experiment is given in Table 35. The conversion, liquid oil yield and mass balance for each experiment are presented in Table 36. If the feed and product weights differed by more than 5% for an experiment, the results were rejected and the test repeated. During the programme, seven of the experiments were repeated at least once.

Conversions varied from 53.27 to 85.31 per cent and liquid oil yields from 24.61 to 63.39 per cent. The maximum liquid yield was obtained at 653 K, 11.1 MPa initial pressure, 0.75 mole fraction of carbon monoxide and 50 min residence time; an 82.90 per cent conversion was obtained at these conditions.

2.2.3 Conversions

Based on the F-statistic at a 95% confidence level, the following model was obtained for conversion as a function of the experimental variables:

$$f = 74.31+5.61X_1+3.15X_2+3.98X_3-2.10X_1X_3-2.76X_1X_2X_3X_4 \quad (3)$$

where f is conversion, as defined in equation (1)

$$X_1 = \frac{T-693\ K}{40\ K}$$

$$X_2 = \frac{y-0.50}{0.25}$$

$$X_3 = \frac{P^o-9.1\ MPa}{2.1\ MPa}$$

$$X_4 = \frac{t-30\ minutes}{20\ minutes}$$

T is reaction temperature in K
y is initial molar fraction of CO in the gas mixture
P^o is initial total pressure in MPa
t is reaction time in minutes

The variables X_1, X_2, X_3, X_4 are defined such that their range is from -1 to +1, based on the levels of the experimental variables studied, T, y, P^o and t. A Student t-test at the 1% level of confidence was used to confirm that little significance was attributed to differences between the predicted and observed data.

Table 34: Feedstock for the experiments without added catalysts

Experiment Number	Treatments	Moisture and Ash Free Lignite g	Moisture (present in lignite) g	Ash (present in lignite) g	Anthracene Oil g	Hydrogen g	Carbon Monoxide g
1	1	30.58	18.19	5.53	86.88	3.46	16.17
2	a	30.67	18.24	5.54	87.12	3.46	16.17
3	b	30.64	18.22	5.54	87.04	1.16	48.01
4	ab	30.59	18.20	5.53	86.90	1.17	48.56
5	c	30.63	18.22	5.53	87.00	5.32	24.85
6	ac	30.66	18.24	5.54	87.10	5.32	27.85
7	bc	30.68	18.23	5.54	87.07	1.89	79.59
8	abc	30.67	18.25	5.54	87.13	1.90	79.80
9	d	30.70	18.26	5.54	87.20	3.48	16.24
10	ad	30.68	18.25	5.54	87.16	3.48	16.24
11	bd	30.64	18.22	5.54	87.04	1.22	51.24
12	abd	30.64	18.22	5.54	87.04	1.55	48.51
13	cd	30.68	18.23	5.54	87.07	5.34	24.92
14	acd	30.65	18.23	5.54	87.00	5.32	24.85
15	bcd	30.65	18.23	5.54	87.07	1.89	79.38
16	abcd	30.64	18.22	5.54	87.04	1.89	79.59
17	central level	30.65	18.23	5.54	87.07	2.97	41.58
18	central level	30.65	18.23	5.54	87.07	2.97	41.58
19	central level	30.65	18.23	5.54	87.07	2.97	41.58

Table 35: Products obtained from treatments without added catalysts

Experiment Number	Treatments	Volume of Gas at Room Temperature and Pressure L	Weight of Gas at Room Temperature and Pressure g	Weight of Aqueous Fraction g	Weight of Filtered Liquid Oil g	Weight of Extracted Liquid Oil g	Weight of Trapped Light Oils plus Water g	Weight of Unextracted and Unconverted Residue g
1	1	63.0	33.51	7.30	64.59	31.83	1.30	19.82
2	a	63.0	30.79	6.63	74.55	26.43	1.03	12.30
3	b	64.5	58.57	5.08	71.32	31.60	2.13	17.07
4	ab	67.0	67.52	4.45	82.37	17.07	2.68	11.97
5	c	97.8	41.27	4.26	80.89	19.76	3.45	12.92
6	ac	99.5	42.69	6.75	70.79	26.96	0.68	13.07
7	bc	99.0	96.44	2.89	80.30	20.24	1.14	16.22
8	abc	116.5	108.50	1.44	78.43	23.57	3.00	10.34
9	d	63.0	46.96	1.50	78.65	16.45	1.68	16.45
10	ad	60.5	41.85	1.97	71.06	23.65	1.36	15.50
11	bd	70.0	70.46	2.00	76.48	24.25	1.39	13.88
12	abd	71.0	82.39	2.64	77.93	16.72	0.39	10.04
13	cd	92.5	52.40	1.06	76.52	26.76	2.69	16.20
14	acd	91.5	53.72	9.12	70.06	24.84	0.10	10.65
15	bcd	96.0	98.67	3.39	85.56	20.94	0.61	10.78
16	abcd	96.0	107.10	1.83	73.18	23.13	0.87	11.16
17	central level	83.0	72.01	2.11	80.54	20.50	0.65	10.83
18	central level	83.0	64.46	1.51	56.63	44.94	2.13	10.75
19	central level	84.0	67.35	1.85	80.10	21.73	2.19	11.78

Table 36: Results of lignite hydrogenolysis without added catalysts

Experiment Number	Treatment	Conversion %	Liquid Oil Yield %	Mass Balance	
				Feed g	Products g
1	1	53.27	33.48	160.80	160.54
2	a	77.96	45.19	161.20	158.85
3	b	62.37	51.83	191.11	189.77
4	ab	78.95	40.98	190.85	183.06
5	c	75.87	44.56	171.55	162.55
6	ac	75.44	34.73	171.71	167.69
7	bc	71.29	43.90	222.97	217.23
8	abc	84.35	48.48	223.29	225.28
9	d	64.46	25.73	161.42	161.09
10	ad	67.54	24.61	161.36	155.39
11	bd	72.78	44.68	195.90	188.46
12	abd	85.31	24.84	191.10	190.30
13	cd	71.41	52.83	171.75	175.63
14	acd	83.33	25.55	171.66	167.49
15	bcd	82.90	63.39	222.76	219.95
16	abcd	81.66	30.25	222.92	217.27
17	central level	82.74	45.58	186.04	186.64
18	central level	83.00	47.31	186.08	180.42
19	central level	79.64	48.16	186.06	185.00

The model is simple, having only three first order effects, a second order effect involving temperature and pressure, and a fourth order effect involving all variables. Time did not seem to be a limiting variable for conversion since its only effect was as part of an interaction with the other three variables. The central point conversion, when $X_1 = X_2 = X_3 = X_4 = 0$, was 74.31%.

Conversion was expressed as a function of one of the experimental variables while keeping the others constant by determining the partial derivative of conversion from equation (3) and then integrating. The results of this analysis are presented in Table 37 where f_2, the conversion at T_2 or P_2^o, is given as a function of f_1 and reaction temperature or initial pressure. The following observations may be made from these results:

(a) increasing temperature tends to increase conversion;

(b) increasing the initial pressure at a CO mole fraction of 0.5 favours an increase in conversion;

(c) observation (b), above, is also valid for a CO mole fraction of 0.25 when both temperature and residence time are either at their high level (733 K, 50 minutes) or low level (653 K, 10 minutes);

(d) at 733 K, residence time of 10 minutes and CO mole fraction of 0.25, an increase in pressure is expected to lower conversions.

At the conditions noted in (d), coking would probably occur thereby lowering conversion as the pressure is increased. The minimum residence time required for gasification of the coke at 733 K was calculated to be 16.4 minutes. This was determined by setting the partial derivative of conversion with respect to pressure equal to zero, while keeping T and y constant. The resulting expression was then solved for t.

2.2.4 Liquid Oil Yields

Model

The results reported as liquid oil yield in Table 36 do not take into account light oils which were removed and trapped with the aqueous phase. Therefore, the values are a lower limit and are

Table 37: Conversion as a function of one experimental variable

T K	y	p^o MPa	t min	f_2 %
variable	0.50	11.1	50	$f_1 + 0.0775\ (T_2-T_1)$
variable	0.50	7.1	10	$f_1 + 0.178\ (T_2-T_1)$
733	0.50	variable	50	$f_1 + 0.00627\ (P_2^o-P_1^o)$
653	0.50	variable	10	$f_1 + 0.0203\ (P_2^o-P_1^o)$
variable	0.25	11.1	50	$f_1 + 0.142\ (T_2-T_1)$
variable	0.25	7.1	10	$f_1 + 0.247\ (T_2-T_1)$
733	0.25	variable	50	$f_1 + 0.0189\ (P_2^o-P_1^o)$
653	0.25	variable	10	$f_1 + 0.0329\ (P_2^o-P_1^o)$
733	0.25	variable	10	$f_1 - 0.00293\ (P_2^o-P_1^o)$

T : reaction temperature (K)
y : initial molar fraction of CO in the gas mixture
p^o : initial total pressure (MPa)
t : reaction time (minutes)
f : conversion (%)

subject to a systematic but irregular error. A statistical model for predicting oil yield will thus be somewhat imprecise.

Based on the F-statistic at a 95% confidence level, the following model was obtained for liquid oil yield as a function of the experimental variables:

$$Y = 39.69 - 5.36\,X_1 + 3.85\,X_2 + 3.27\,X_3 - 3.20\,X_4 - 2.05\,X_1X_2 - 2.85\,X_1X_3 - 4.81\,X_1X_4 + 3.25\,X_3X_4 + 3.11\,X_1X_2X_3 - 2.08\,X_1X_3X_4 - 1.51\,X_1X_2X_3X_4 \quad (4)$$

where Y is liquid oil yield, as defined in equation (2)

and X_1, X_2, X_3, X_4 are variables defined in equation (3)

The model is obviously complex, involving first, second, third and fourth order interactions. The central point liquid oil yield, when $X_1 = X_2 = X_3 = X_4 = 0$, was 39.69%.

Oil Yield as a Function of One Variable

Liquid oil yield was expressed as a function of one of the experimental variables while keeping the others constant using the same method described in the previous section. The results of this analysis are presented in Table 38.

Examples 1 to 4 show that lower temperatures would favour higher oil yields at 11.1 MPa, residence time of 50 minutes and CO mole fraction of 0.25 or 0.50. However, higher temperatures favour higher oil yields at 7.1 MPa and 10 minutes reaction time. The critical times at 7.1 MPa for which the tendency would be reversed was calculated as 11.6 minutes for y equal to 0.50 and 42.4 minutes for y equal to 0.25. These values were determined by setting the partial derivative of liquid oil yield, with respect to temperature, equal to zero while keeping P^o and y constant, and solving the resultant expression for t. Therefore, between a 10 and 11.6 minute residence time (for y = 0.50) or 42.4 minute residence time (for y = 0.25), higher temperatures would produce higher yields. For greater residence times, lower temperatures would be required to increase oil yields.

A fourfold increase in time would be required to reverse the temperature effect if the initial CO mole fraction was halved from 0.5 to 0.25. The important role of CO for liquefaction of oxygenated coals is therefore illustrated.

Table 38: Liquid oil yield as a function of one experimental variable

Example Number	T K	y	p^o MPa	t min	f_2 %
1	variable	0.50	11.1	50	$f_1 - 0.378\ (T_2-T_1)$
2	variable	0.50	7.1	10	$f_1 + 0.00550\ (T_2-T_1)$
3	variable	0.25	11.1	50	$f_1 - 0.366\ (T_2-T_1)$
4	variable	0.25	7.1	10	$f_1 + 0.172\ (T_2-T_1)$
5	733	0.50	variable	50	$f_1 + 0.00530\ (P_2^o-P_1^o)$
6	653	0.50	variable	10	$f_1 + 0.00263\ (P_2^o-P_1^o)$
7	733	0.25	variable	50	$f_1 - 0.0000333\ (P_2^o-P_1^o)$
8	653	0.25	variable	10	$f_1 + 0.180\ (P_2^o-P_1^o)$

T : reaction temperature (K)

y : initial molar fraction of CO in the gas mixture

p^o : initial total pressure (MPa)

t : reaction time (minutes)

f : conversion (%)

This effect can also be seen for the case when temperature is kept constant. Examples 5 and 6 (in Table 38) indicate that an increase in pressure for y equal to 0.50 would increase oil yield, probably by favouring equilibrium reactions toward oil formation. However, this effect would be changed when the initial CO mole fraction is 0.25. In the latter case (as shown in examples 7 and 8), at the higher temperature and residence time, increasing pressure would slightly decrease oil yields. At the lower temperature and residence time, increasing pressure would increase oil yields at least an order of magnitude greater than if y was 0.50.

These results illustrate the complexity of the reactions occurring during hydrogenolysis. The competition between coke formation, liquid formation and gasification is highly sensitive to temperature but less sensitive to pressure. As well, residence time seems to affect oil formation to a greater degree than it affects conversion.

Oil Yield as a Function of Temperature, Pressure and Reaction Time

In this section, the combined effect of temperature, pressure and reaction time on liquid oil yield will be examined for two cases: when the initial mole fraction of CO is 0.50 and 0.25. However, for this analysis, deviations around the central point liquid oil yield will be studied rather than deviations from the low to high level of the experimental variables. This should minimize greater errors associated with prediction of combined effects.

Recall that the central point conditions are as follows:

reaction temperature (T): 693 K
initial pressure at room temperature (P^o): 9.1 MPa
initial molar fraction of CO (y): 0.50
residence time at reaction temperature (t): 30 minutes
predicted liquid oil yield (Yo): 39.69%

If T, P^o or t are changed from the central point level while keeping y constant, the change in predicted liquid oil yield can be expressed as follows:

$$Y = Yo + dY$$

or

$$Y = Yo + \frac{\partial Y}{\partial T} dT + \frac{\partial Y}{\partial P^o} dP^o + \frac{\partial Y}{\partial t} dt \qquad (5)$$

where $\frac{\partial Y}{\partial T} = -0.134 - 0.0713 X_3 - 0.120 X_4 - 0.0520 X_3X_4$

$$\frac{\partial Y}{\partial P^o} = 0.0109 - 0.00950 X_1 + 0.0108 X_4 - 0.00693 X_1X_4$$

$$\frac{\partial Y}{\partial t} = -0.160 - 0.241 X_1 + 0.163 X_3 - 0.104 X_1X_3$$

The partial derivatives were calculated from equation (4).

The effect of central point deviations of the experimental conditions at y equal to 0.50 is shown in Table 39. The first seven examples involve increasing the severity of the operating conditions, the next seven, decreasing the operating conditions and the last five involves both.

The statistical model predicts that positive deviations in pressure (examples 3 and 4) and negative deviations in temperature (example 8) will increase liquid oil yields. As well, increasing residence time at high pressures (examples 3, 4, 17 and 18) but decreasing residence time at lower pressures (examples 8, 9, 11, 14) will increase liquid oil yield. The predicted optimum conditions at an initial CO fraction of 0.50 are as follows:

reaction temperature (T): 653 K
initial total pressure (P^o): 11.1 MPa
reaction time (t): 50 minutes

The effect of operating conditions at a CO mole fraction of 0.25, which is often found in synthesis gas, is shown in Table 40. The trends in predicted oil yield are similar to those found for y equal to 0.50. However, the effect of residence time is more pronounced when y is equal to 0.25, as shown in examples 14, 17, 18 and 19 of tables 39 and 40.

The predicted optimum operating conditions with a constrained temperature were calculated using an optimization technique. The results, presented in Table 41, confirm previously described trends. Optimum yields are generally found at a high CO concentration, pressure and residence time and a low temperature. However, when temperature cannot be lower than 693 K, shorter residence times and high temperatures increase liquid oil yields. At high temperatures, liquid oils are probably rapidly formed and thus, to minimize gasification, short reaction times are required.

Table 39: Effect of operating conditions on predicted liquid oil yields at a CO mole fraction of 0.50

Example Number	T K	p^o MPa	t min	Y %	Deviation of Y from central point Yo %
1	733	9.1	30	34.33	-5.36
2	693	9.1	50	36.49	-3.20
3	693	11.1	30	42.96	+3.27
4	693	11.1	50	46.27	+6.57
5	733	11.1	30	31.90	-7.79
6	733	9.1	50	21.51	-18.18
7	733	11.1	50	19.34	-20.35
8	653	9.1	30	45.05	+5.36
9	693	9.1	10	42.89	+3.20
10	693	7.1	30	36.42	-3.27
11	693	7.1	10	46.12	+6.43
12	653	7.1	30	36.08	-3.61
13	653	9.1	10	38.63	-1.06
14	653	7.1	10	42.40	+2.71
15	693	7.1	50	26.72	-12.97
16	693	11.1	10	39.66	-0.03
17	653	11.1	30	48.32	+8.63
18	653	11.1	50	63.32	+23.63
19	653	11.1	10	34.86	-4.83

T : reaction temperature (K)
p^o : initial total pressure (MPa)
t : reaction time (minutes)
y : predicted liquid oil yield (%)

Table 40: Effect of operating conditions on predicted liquid oil yields at a CO mole fraction of 0.25

Example Number	T K	p^o MPa	t min	Y %	Deviation of Y from central poind Yo %
1	733	9.1	30	36.38	-3.31
2	693	9.1	50	36.49	-3.20
3	693	11.1	30	42.96	+3.27
4	693	11.1	50	46.26	+6.57
5	733	11.1	30	27.73	-11.96
6	733	9.1	50	23.56	-16.13
7	733	11.1	50	19.70	-19.99
8	653	9.1	30	43.00	+3.31
9	693	9.1	10	42.89	+3.20
10	693	7.1	30	36.42	-3.27
11	693	7.1	10	46.12	+6.43
12	653	7.1	30	27.81	-11.88
13	653	9.1	10	36.58	-3.11
14	653	7.1	10	29.60	-10.09
15	693	7.1	50	26.72	-12.97
16	693	11.1	10	39.66	-0.03
17	653	11.1	30	58.19	+18.50
18	653	11.1	50	72.82	+33.13
19	653	11.1	10	43.56	+3.87

T : reaction temperature (K)
p^o : initial total pressure (MPa)
t : reaction time (minutes)
Y : predicted liquid oil yield (%)

Table 41: Predicted optimum operating conditions for liquid oil yields with a constrained temperature

Temperature Range K	Optimum Operating Conditions			
	T K	y	p^o MPa	t min
653-733	653	0.75	11.1	50
673-733	673	0.75	11.1	50
693-733	733	0.75	11.1	10
693	693	0.75	11.1	50

T : reaction temperature (K)

y : initial mole fraction of CO in the gas mixture

p^o : initial total pressure (MPa)

t : reaction time (minutes)

Since a number of experimental errors occur when recovering liquid oils, the yields given in tables 39 to 41 may not be the values obtained during actual experimentation. However, this should not alter the ability of the model to predict trends.

2.2.5 Elemental Composition of Liquid Oil Products

The elemental composition of liquid oil products recovered from the reaction mixture by filtration and benzene extraction is given in Table 42. As well, the elemental composition of the feedstock which was calculated from the results obtained with lignite and anthracene oil is included for comparative purposes. The results for each sample may not add up to exactly 100.0%. This is due to errors associated with the analysis procedure.

The hydrogen content of the liquid oils varied from 5.6 to 6.4% by weight, which shows that hydrogenation of the feedstock occurred during every experiment.

The oxygen content was substantially decreased from 7.9% to 2.0-3.6%, but not to the level of anthracene oil, which was 1.8%.

The nitrogen content varied from 0.8 to 1.0% and the sulphur content from 0.3 to 0.5%; these values are not significantly different from the nitrogen and sulphur content of the feed. Variations in the results may be due to experimental error.

The carbon content seems to have increased slightly from 84.0% to 86.8-92.4%.

The effect of varying operating conditions on hydrogen and oxygen content is presented in tables 43 to 46. The results in Table 43 show that greater hydrogenation occurs at the lower temperature, 653 K. However, the oxygen content is also highest at this temperature which indicates that the deoxygenation capacity of the ash fraction improves at higher temperatures. Reaction time, initial CO/H_2 ratio and total initial pressure did not seem to have a predominant effect, as shown in tables 44 to 46. Increasing these last parameters tended to lower hydrogen and oxygen content during some of the experiments but increase them during others. Therefore, temperature was the variable which most affected elementary composition.

Table 42: Elemental composition[1] of liquid products and feedstock

Experiment Number	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur
1	90.1	6.1	3.1	0.8	0.5
2	89.8	5.9	2.5	0.9	0.4
3	86.8	5.9	2.8	0.9	0.4
4	89.8	5.6	2.1	0.9	0.3
5	92.3	6.3	2.7	1.0	0.3
6	87.5	5.8	2.1	0.8	0.3
7	88.9	6.1	3.2	0.8	0.4
8	90.0	6.1	2.1	0.9	0.4
9	90.9	6.4	3.6	1.0	0.5
10	89.2	5.9	2.1	0.8	0.3
11	90.1	6.0	2.8	0.9	0.4
12	89.7	5.6	2.1	0.8	0.3
13	90.1	6.3	3.2	0.9	0.4
14	87.1	6.0	2.1	0.8	0.3
15	92.4	6.6	2.9	1.0	0.4
16	92.2	6.1	2.0	0.9	0.3
central point average	88.3	6.1	2.6	0.9	0.4
feedstock[2]	84.0	5.4	7.9	0.9	0.5

[1] per cent by weight, as received

[2] per cent by weight, moisture and ash free basis

Table 43: Effect of reaction temperature on the hydrogen and oxygen contents of the liquid products

Experiment Numbers	p^o MPa	CO/H_2 molar ratio	t min	Hydrogen (weight %) at 653 K	at 693 K	at 733 K	Oxygen (weight %) at 653 K	at 693 K	at 733 K
1, 2	7.1	0.33/1	10	6.1	-	5.9	3.1	-	2.5
3, 4	7.1	3/1	10	5.9	-	5.6	2.8	-	2.1
5, 6	11.1	0.33/1	10	6.3	-	5.8	2.7	-	2.1
7, 8	11.1	3/1	10	6.1	-	6.1	3.2	-	2.1
9, 10	7.1	0.33/1	50	6.4	-	5.9	3.6	-	2.1
11, 12	7.1	3/1	50	6.0	-	5.6	2.8	-	2.1
13, 14	11.1	0.33/1	50	6.3	-	6.0	3.2	-	2.1
15, 16	11.1	3/1	50	6.6	-	6.1	2.9	-	2.0
17, 18, 19	9.1	1/1	30	-	6.1	-	-	2.6	-

p^o : initial pressure at room temperature

t : reaction time

Table 44: Effect of reaction time on the hydrogen and oxygen contents of the liquid products

Experiment Numbers	T K	P^o MPa	CO/H_2 molar ratio	Hydrogen (weight %) at 10 min	at 30 min	at 50 min	Oxygen (weight %) at 10 min	at 30 min	at 50 min
1, 9	653	7.1	0.33/1	6.1	-	6.4	3.1	-	3.6
2, 10	733	7.1	0.33/1	5.9	-	5.9	2.5	-	2.1
3, 11	653	7.1	3/1	5.9	-	6.0	2.8	-	2.8
4, 12	733	7.1	3/1	5.6	-	5.6	2.1	-	2.1
5, 13	653	11.1	0.33/1	6.3	-	6.3	2.7	-	3.2
6, 14	733	11.1	0.33/1	5.8	-	6.0	2.1	-	2.1
7, 15	653	11.1	3/1	6.1	-	6.6	3.2	-	2.9
8, 16	733	11.1	3/1	6.1	-	6.1	2.1	-	2.0
17, 18, 19	693	9.1	1/1	-	6.1	-	-	2.6	-

T : reaction temperature

P^o : initial pressure at room temperature

Table 45: Effect of initial gas composition on the hydrogen and oxygen contents of the liquid products

Experiment Numbers	T K	p^o MPa	t min	Hydrogen (weight %)			Oxygen (weight %)		
				0.33 CO/H_2	1 CO/H_2	3 CO/H_2	0.33 CO/H_2	1 CO/H_2	3 CO/H_2
1, 3	653	7.1	10	6.1	-	5.9	3.1	-	2.8
2, 4	733	7.1	10	5.9	-	5.6	2.5	-	2.1
5, 7	653	11.1	10	6.3	-	6.1	2.7	-	3.2
6, 8	733	11.1	10	5.8	-	6.1	2.1	-	2.1
9, 11	653	7.1	50	6.4	-	6.0	3.6	-	2.8
10, 12	733	7.1	50	5.9	-	5.6	2.1	-	2.1
13, 15	653	11.1	50	6.3	-	6.6	3.2	-	2.9
14, 16	733	11.1	50	6.0	-	6.1	2.1	-	2.0
17, 18, 19	693	9.1	30	-	6.1	-	-	2.6	-

T : reaction temperature

p^o : initial pressure at room temperature

t : reaction time

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Table 46: Effect of initial cold pressure on the hydrogen and oxygen contents of the liquid products

Experiment Numbers	T K	CO/H_2 molar ratio	t min	Hydrogen (weight %) at 7.1 MPa	Hydrogen (weight %) at 9.1 MPa	Hydrogen (weight %) at 11.1 MPa	Oxygen (weight %) at 7.1 MPa	Oxygen (weight %) at 9.1 MPa	Oxygen (weight %) at 11.1 MPa
1, 5	653	0.33/1	10	6.1	-	6.3	3.1	-	2.7
2, 6	733	0.33/1	10	5.9	-	5.8	2.5	-	2.1
3, 7	653	3/1	10	5.9	-	6.1	2.8	-	3.2
4, 8	733	3/1	10	5.6	-	6.1	2.1	-	2.1
9, 13	653	0.33/1	50	6.4	-	6.3	3.6	-	3.2
10, 14	733	0.33/1	50	5.9	-	6.0	2.1	-	2.1
11, 15	653	3/1	50	6.0	-	6.6	2.8	-	2.9
12, 16	733	3/1	50	6.3	-	6.1	2.1	-	2.0
17, 18, 19	683	1/1	30	-	6.1	-	-	2.6	-

T : reaction temperature

t : reaction time

In the previous section, the highest liquid oil yields were observed to occur at the low temperature and high residence time. Hydrogenation also occurred at the low temperature but high residence times were not required. This is illustrated by the results of experiments 7 and 15 which were both conducted at 380 K, 11.1 MPa and a CO/H_2 ratio of 3/1, but 7 was run for 10 minutes while 15 was run for 50 minutes; experiments 7 and 15 produced liquid oil yields of 43.9 and 63.4% having hydrogen contents of 6.1 to 6.6% respectively. Therefore, an increase in residence time seems to increase solubilization to improve liquid yields but does not substantially increase hydrogenation. This last reaction occurs very rapidly during the initial stages of liquefaction.

2.2.6 Gas Composition

The final gas composition and pressure for each experiment is presented in Table 47. The main components in the gas were hydrogen, carbon monoxide, carbon dioxide and methane. Smaller quantities (< 2% by volume) of ammonia and higher molecular weight hydrocarbons were detected as well. The higher concentrations of CO and lower concentrations of H_2 occurred when the initial CO/H_2 ratio was high. Thus, a substantial portion of the reactant gases were not converted.

Table 48 presents the evolution of the CO/H_2 molar ratio as a function of reaction time for each experiment. No distinct regular pattern was observed. As well, the values at time zero were not always the same for experiments which were subjected to supposedly identical heating rates. These might be an indication of the high sensitivity of gas forming reactions to variations in experimental conditions. For instance, heating the autoclave beyond the reaction temperature, even for a few minutes, may trigger a series of reactions which would otherwise not occur.

Maxima and minima of the CO/H_2 ratio were observed. This suggests that various reaction mechanisms predominate during the different phases of liquefaction.

The change in gas composition with reaction time for every experiment is given in Appendix 2.

Table 47: Final gas composition for experiments without added catalysts (% by volume)

Experiment Number	Treatment	Final Pressure[1] MPa	Hydrogen	Carbon Monoxide	Carbon Dioxide	Ammonia	Methane	Two-carbon Hydrocarbons	Three-carbon Hydrocarbons	Four-carbon Hydrocarbons	Higher Molecular Weight Hydrocarbons
1	1	19.3	71.88	21.09	6.30	-	0.14	0.39	-	0.20	-
2	a	22.0	68.5[illegible]	16.28	9.91	0.09	3.25	1.15	0.57	0.08	0.15
3	b	20.9	32.03	53.33	14.04	0.07	0.23	0.13	0.03	0.07	0.07
4	ab	22.3	26.73	48.47	20.92	-	2.38	0.86	0.38	0.15	0.11
5	c	29.8	71.60	23.50	4.81	-	-	0.06	-	0.03	-
6	ac	31.9	71.27	19.65	6.05	0.08	1.75	0.67	0.40	0.13	-
7	bc	30.4	71.24	22.00	6.28	-	0.38	0.28	-	0.20	-
8	abc	32.6	26.49	61.19	9.44	0.12	1.89	0.56	0.22	0.04	0.05
9	d	29.1	50.02	20.12	20.37	0.03	6.26	1.20	1.20	0.60	0.20
10	ad	22.3	55.94	12.36	21.36	0.03	6.26	1.87	1.27	0.62	0.29
11	bd	20.6	24.39	56.58	17.62	0.30	0.60	0.23	0.10	0.10	0.08
12	abd	22.7	22.85	29.89	37.91	-	5.54	1.85	0.91	0.51	0.54
13	cd	29.2	63.93	21.02	14.02	-	0.51	0.31	0.13	0.08	-
14	acd	32.2	57.70	23.27	8.20	-	6.70	1.73	1.04	0.79	0.60
15	bcd	29.1	23.32	57.56	18.20	0.15	0.43	0.15	0.03	0.03	0.13
16	abcd	31.3	21.56	44.87	28.67	0.30	2.68	0.95	0.50	0.19	0.28
17	central level	26.0	40.97	35.73	19.95	0.62	1.59	0.52	0.26	0.16	0.20
18	central level	24.6	46.13	33.29	18.44	0.26	0.92	0.53	0.16	0.11	0.16
19	central level	25.6	46.90	31.41	18.46	0.39	1.07	0.72	0.39	0.27	0.39

[1] at reaction temperature

Table 48: Evolution of the CO/H_2 molar ratio during liquefaction

Experiment Numbers	Treatment (excluding time)	CO/H_2 molar ratio at 0[1] min	at 0[2] min	at 5 min	at 10 min	at 25 min	at 30 min	at 40 min	at 50 min
1, 9	1	0.47	0.25	0.33	0.29	0.32	0.44	-	0.40
2, 10	a	0.33	0.33	0.28	0.24	0.31	-	0.22	0.33
3, 11	b	3.15	3.53	-	1.67	2.01	-	2.32	3.53
4, 12	ab	2.81	2.50	0.43	1.81	0.43	-	-	1.31
5, 13	c	0.65	0.33	0.48	0.33	0.29	0.35	0.30	0.33
6, 14	ac	0.18	0.40	0.52	0.28	0.27	0.20	0.21	0.40
7, 15	bc	2.63	3.19	-	2.77	2.72	2.72	-	2.47
8, 16	abc	2.72	3.31	2.15	2.31	2.80	2.80	2.31	2.08

[1] experiments 1 to 8

[2] experiments 9 to 16

2.2.7 Viscosity of Liquid Products

The viscosity of anthracene oil and a number of the liquid oil products at 333 K are presented in Table 49. All products had a low viscosity (11 to 24 cs) which allowed easy handling of the mixture, but not as low as the viscosity of anthracene oil (6 cs). Thus, the high fluidity of the liquid products was mainly due to the anthracene oil.

2.3 Experiments with Added Catalysts

The characteristics of the four catalysts used for this study are given in Table 50. The first (MB 306) was a cobalt molybdate catalyst on alumina supplied by EMR. The second (MB 289) was similar to the first, but contained 7.32% potassium carbonate promotor. The other two catalysts were nickel and iron on peat char, supplied by the University of Sherbrooke.

Table 51 presents the quantity of each component of the feedstock. The weight of each product, conversions and liquid oil yields are presented in Table 52. The data from experiment 19 without added catalysts is included for comparative purposes. Experiments 20 to 23 were primary conversions of raw lignite and experiments 24 to 27 were secondary conversions of the liquid oil product obtained at central level conditions described in previous sections.

The results from experiments 19 to 23 show that the addition of the catalysts did not appear to affect conversions or liquid oil yields. However, a significant quantity of light oils were observed to vapourize during product recovery. Thus, it is likely that the catalysts used increased the light oil fraction and may have even increased total liquid oil yield.

When the liquid oil product obtained at central level reaction conditions was hydrogenolysed in the presence of a catalyst, five to seven per cent of the oil was converted to char.

The elementary composition of the liquid oils obtained from catalytic liquefaction is given in Table 53. Compared with liquefaction without added catalysts, only one of the catalysts (potassium promoted cobalt-molybdate) seemed to produce an oil of higher hydrogen content. However the increase was only by 0.3%.

Secondary catalytic treatment of the product oil did not seem to increase the hydrogen content. All catalysts seemed to cause a slight decrease (0.1 to 0.5%) in oxygen content. However, during the final tasks of the

Table 49: Viscosity[1] of liquid oil products

Liquid Product Number[2]	Treatment	Viscosity cs
3	b	15.2
5	c	18.8
6	ac	14.9
7	bc	22.1
8	abc	11.6
9	d	23.8
10	ad	19.7
11	bd	22.0
12	abd	21.5
16	abcd	14.1
anthracene oil	-	6.0

[1] measured at 333 K

[2] refers to experiment number

Table 50: Characteristics of catalysts used for catalytic liquefaction

Catalyst	Composition: Metal Compounds (weight per cent)	Composition: Support	Surface Properties: Surface Area (m^2/g)	Surface Properties: Pore Volume (cm^3/g)
MB 306[1]	CoO: 1.17 MoO_3: 2.08	alumina	233	0.519
MB 289[1]	CoO: 1.16 MoO_3: 2.05 K_2CO_3: 7.32	alumina	189	0.511
Ni^{+2}on C[2]	Ni: 1.04	peat char	-	-
Fe^{+3}on C[2]	Fe: 2.09	peat char	-	-

[1] prepared by Energy, Mines and Resources Canada supplied by the Scientific Authority

[2] prepared and supplied by the chemical engineering department of the University of Sherbrooke

Table 51: Feedstock[1] for the experiments with added catalysts

Experiment Number	Organic Fraction[2] g	Moisture[3] g	Ash[3] g	Anthracene Oil g	Catalyst Type	Catalyst Weight g
19	30.65	18.23	5.54	87.07	-	-
20	30.64	18.23	5.54	87.05	MB 306	5.00
21	30.65	18.23	5.54	87.07	MB 289	5.00
22	30.65	18.23	5.54	87.07	Ni^{+2}/C	4.29
23	30.65	18.23	5.54	87.07	Fe^{+3}/C	1.52
24	49.91	-	-	-	MB 306	2.33
25	49.79	-	-	-	MB 289	2.33
26	49.81	-	-	-	Ni^{+2}/C	2.05
27	49.90	-	-	-	Fe^{+3}/C	0.98

[1] includes 3.0 g H_2 and 41.6 g CO

[2] for experiments 19 to 23, moisture and ash free lignite; for experiments 24 to 27, liquid oil product from a previous experiment without added catalysts

[3] naturally occurring in lignite

Table 52: Products obtained from experiments with added catalysts[1]

Experiment Number	Volume of Gas	Final Pressure	Aqueous Fraction	Filtered Liquid Oil	Extracted Liquid Oil	Trapped Light Oils plus Water	Unextracted and Unconverted Residue	Conversion	Liquid Oil Yield
	L	MPa	g	g	g	g	g	%	%
19	84.0	25.6	1.85	80.10	21.73	2.19	11.78	79.64	48.16
20	83.0	25.6	2.11	83.86	17.37	1.04	16.29	81.20	46.28
21	84.0	25.5	0.79	79.65	21.55	1.25	15.66	83.30	46.10
22	84.0	24.9	1.70	77.22	24.87	2.30	14.89	83.50	49.00
23	84.0	24.9	1.70	73.45	26.28	2.40	13.35	79.50	41.31
24	55.8	20.1	-	46.92	-	-	4.14	94.00	-
25	61.7	20.1	-	47.15	-	-	3.82	94.70	-
26	62.4	19.8	0.30	47.32	-	-	3.30	95.00	-
27	68.1	20.1	-	46.41	-	-	2.72	93.00	-

[1] reaction conditions - temperature : 693 K
initial pressure at room temperature: 9.1 MPa
initial CO/H_2 ratio : 1/1
residence time : 30 minutes

Table 53: Ultimate analysis of liquid products from catalytic liquefaction

Experiment Number	Elemental Composition (% weight)				
	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur
19	88.3	6.1	2.6	0.9	0.4
20	89.3	6.1	2.4	0.9	0.4
21	88.7	6.4	2.4	0.9	0.3
22	90.4	6.1	2.1	0.9	0.4
23	88.6	6.0	2.4	0.9	0.4
24	88.3	6.2	2.3	0.8	0.4
25	90.0	6.0	2.3	0.9	0.3
26	91.2	6.2	2.5	0.9	0.3
27	89.3	6.0	2.1	0.9	0.5

project, the oxygen content of the oils were observed to increase to an equilibrium level when exposed to air. For example, three samples of the product obtained from experiment 22 were initially found to contain 1.9% oxygen. Two days later, two other samples of the same product were found to contain 2.4% oxygen (the average is reported in Table 53). It is likely that during product upgrading and storage, oxygen from the air reacts with and dissolves in the product oil. Thus, the reported values for oxygen content may be higher than the true values. During future work, more care should be taken to avoid oxygen contact with the oil.

No significant denitrification or desulphurization occurred during the reaction. However, this may be due to the already low nitrogen (0.9 - 1.2%) and sulphur (0.4 - 0.6%) contents in the feed.

The change in gas composition with reaction time is given in Appendix 2. The final gas composition after each experiment is presented in Table 54. There is no significant difference between the results of experiment 19 and those of 20 to 23. Thus, adding the catalysts for primary conversion did not affect final gas composition which was approximately 50% H_2, 25% CO, 18% CO_2, 1% CH_4 and 6% others. However, when liquid products from primary conversion were hydrogenolysed, 98% of the final gas was approximately equal volumes of hydrogen and carbon monoxide. This was nearly identical to the initial gas composition which suggests that little hydrogenation or deoxygenation occurred compared to primary conversion.

Table 54: Final gas composition from catalytic liquefaction

Experiment Number	Gas Composition (% volume)									
	Hydrogen	Carbon Monoxide	Carbon Dioxide	Methane	C_2 Hydro-carbons	C_3 Hydro-carbons	C_4 Hydro-carbons	$>C_4$ Hydro-carbons	Ammonia	unidentified
19	46.90	31.41	18.46	1.07	0.72	0.39	0.27	0.39	0.39	-
20	45.35	31.99	16.21	1.03	0.32	-	-	-	-	5.10
21	57.71	20.74	18.68	1.54	0.37	0.10	-	-	-	0.86
22	52.22	27.33	18.17	1.31	0.12	-	-	-	-	0.85
23	50.16	29.39	17.68	1.05	0.51	0.13	-	-	-	1.08
24	56.24	40.90	0.82	0.56	0.11	-	-	-	0.36	1.00
25	51.63	46.44	0.86	0.30	0.09	-	-	0.08	-	0.60
26	51.06	46.99	0.88	0.38	-	-	-	0.11	-	0.58
27	45.59	52.15	0.61	0.57	0.16	-	-	0.17	-	0.76

CHAPTER 3

EQUILIBRIUM THERMODYNAMICS

1.0 BACKGROUND

The equilibrium composition of a multiphase mixture under given conditions of high temperature and pressure can be determined by calculating the chemical potential or mixture fugacity of each of the components in all the phases present. The potential practical application of the results requires that all models based on ideal behaviour be abandoned and more realistic approaches sought. This does not present a serious problem in the case of a system with only a gaseous phase present. Here the method of corresponding states, modified through the inclusion of simple mixing rules, provides a promising starting point. The real problem arises when the possibility of one or more liquid phases is admitted, since there is no simple method for calculating chemical potentials for such systems.

Although studies on the computation of complex chemical equilibria have been extensively conducted, (Van Zeggeren and Storey, 1970; Zeleznik and Gordon, 1968) few have dealt with energy conversion reactions. Only one was found dealing with this subject to date.

The equilibrium product distribution was computed (Kaufman and Weiss, 1975) for a cellulose liquefaction process in order to obtain information on the effects of the following parameters on the reaction: temperature, pressure, and reactant composition. Computation was done in the temperature range of 600 to 1000 K and pressure range of 5 to 10 MPa. Cellulose was taken as $C_6H_{10}O_5$ and various initial compositions of the reactant gases were used to study the product compositions at equilibrium. A computer program devised by Ma and Shipman (1972) was used for these calculations.

The results of that study were subject to two major sources of error:

(a) the gases were assumed to behave ideally which was an over-simplification since computations were done for a high pressure range (> 5 MPa);

(b) the effect of the presence of liquid organic compounds or liquid water was ignored; only two phases were assumed present at equilibrium, a gaseous mixture and solid carbon; this fact would introduce a large error in chemical equilibria calculations since the main products of a liquefaction process are liquids.

Numerous methods have been developed to calculate phase data for non-ideal vapour-liquid equilibria of various mixtures. Thus, the extension of these methods for the simultaneous study of both vapour-liquid and chemical equilibria is probably the most promising approach to study the thermodynamics of non-ideal systems.

Methods for high-pressure vapour-liquid equilibria have been roughly classified into two groups. Firstly, the phase equilibria may be calculated from an equation of state which is applicable to both the vapour and liquid phases. A second procedure is based on utilizing separate equations for each phase; an equation of state is used for expressing vapour phase behaviour and a semi-empirical equation for activity coefficients is employed for the liquid phase.

In the present work, two equations seemed applicable: the Wilson equation for calculating liquid activity coefficients and the Redlich-Kwong equation of state.

2.0 APPLICABLE THERMODYNAMIC RELATIONS

2.1 Wilson Model Equation

Model equations are obtained from a theory of solutions which has been parameterized and fitted to experimental phase data. The Wilson equation, based on a semi-empirical generalization of the Flory-Huggins theory of solutions, is one of the simplest and most successful examples of this approach. The end product of this process is an expression for the activity coefficient of a liquid component in terms of as many disposable parameters as there are components in the mixture. These parameters are obtained through a least squares fit to experimental data, on the assumption that the vapour behaves as an ideal gas. Unfortunately, this last feature limits the method to low pressure conditions. The equation is further limited by the lack of any method for estimating the effect of temperature on the Wilson constants.

The performance of the Wilson equation has been very impressive in the limited range of temperature and pressure where it has been applied. The problem with the pressure limitation is artificial, since the assumption of ideal behaviour for the vapour is one of convenience rather than necessity, but the temperature dependence of the constants remains a problem.

The Wilson equation approach could have been the best for the present investigation. However, it was abandoned since its adaption would probably have required more time than was available.

2.2 Redlich-Kwong Equation of State

2.2.1 Fugacity

The Redlich-Kwong (R-K) equation of state for a pure component is expressed as follows:

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v+b)} \qquad (6)$$

where, P, T and v are, respectively, the pressure, temperature and molar volume of the system. The constants a and b are the Redlich-Kwong constants, which were originally determined using the standard criterion for a critical state.

The foundation of this approach is the assumption that the R-K equation is an acceptably accurate equation of state for both the gaseous and the liquid phases. The advantage accrued from this assumption is a common reference state for the free energy of both the liquid and vapour phases. The previous equation is cubic in the molar volume v and thus has three roots for given values of temperature and pressure. If only a gaseous phase exists, then the largest root, the molar volume of the gas phase, will be real and positive, whereas the other two roots will be complex. If both gaseous and liquid phases are present, then both the highest and the lowest roots will be real and positive, with the lowest root being the molar volume of the liquid phase.

Once the equation of state has been established the fugacity of the system may readily be calculated using the well known methods of thermodynamics. Specifically, the fugacity coefficient is given by

$$RT\ln\phi = \int_{v}^{\infty}\left[\left(\frac{\partial P}{\partial n}\right)_{T,v} - \frac{RT}{v}\right]dV - RT\ln\left(\frac{Pv}{RT}\right) \qquad (7)$$

where V is the total volume

The following is obtained by substituting for P from equation (6):

$$\ln\phi = \ln\{RT/P(v-b)\}+Pv/RT-1-(a/RT^{3/2}b)\ln\{(\frac{v+b}{v})\} \qquad (8)$$

2.2.2 Estimation of a and b for a pure substance

The object is to calculate a and b using experimental data. The data in question are the liquid's molar volume and vapour pressure at some given temperature, T.

The vapour pressure, P, and the liquid molar volume are substituted into equation (6) to yield a relation between a and b. The next step is to invoke the vapour-liquid equilibria, which requires ϕvapour = ϕliquid. The application of this condition by means of equation (8) presents a difficulty, since the molar volume of the vapour is required, which in turn requires values of a and b. To circumvent this obstacle, the following procedure was adopted. A value of b (0.04) was selected, a was then calculated from equation (6), then equation (6) solved for the molar volume of the gas (of course it also gives the known molar volume of the liquid as the lowest root). From this ϕ^V and ϕ^L were calculated as a function of a (using the assumed value of b) and a calculated from the

equilibrium condition. This value of a was compared with that originally calculated from the R-K equation. If these two estimates for a did not agree, b was adjusted and the process repeated until they did agree to some prescribed level of accuracy.

2.2.3 Extension to Mixtures

The method can be extended to include mixtures through the (arbitrary) addition of mixing rules. If y and x are the mole fractions of the gaseous and liquid phases, respectively, then

$$a_G = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i a_{ij} y_j \qquad \text{Gas}$$

$$a_L = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i a_{ij} x_j \qquad \text{Liquid}$$

$$b_G = \sum_{i=1}^{N} y_i b_i \qquad \text{Gas}$$

$$b_L = \sum_{c=1}^{N} x_i b_i \qquad \text{Liquid}$$

for an N component mixture.

The coefficients a_{ii} and b_i are simply a and b for the pure substance i. The cross terms a_{ij} are often estimated as a geometric mean:

$$a_{ij} = \sqrt{a_{ii} a_{jj}}$$

It has been reported (Redlich and Kwong, 1949) that an appreciable improvement in the performance of the theory can be achieved by the addition of one further empirical constant, which is estimated by calibrating the method against experimental data for mixtures. This extra parameter, Θ, appears in the cross term:

$$a_{ij} = (1-\Theta_{ij}) \sqrt{a_{ii} a_{jj}}$$

Values for Θ_{ij} are available for a few binary mixtures

2.2.4 Temperature Dependence of the R-K Parameters

That the R-K parameters are strongly temperature dependent may be demonstrated by repeating their calculation, described above, using vapour pressures for a range of temperature. This problem has recently received a detailed study and a reliable method was devised for calculating the R-K constants in terms of the reduced temperature (Hirata et al., 1975).

To summarize, the R-K method appears to provide a relatively straightforward method for the calculation of both liquid and gas phase chemical potentials at high pressures and relatively high temperatures. Accordingly, it was decided to adopt this approach in the development of a thermodynamic model for coal liquefaction.

3.0 SOLUTION OF COMPLEX EQUILIBRIA BY OPTIMIZATION

3.1 Application to Chemical Equilibria

The thrust of the present approach is to derive an expression for the free energy of a multicomponent system as a function of the ambient pressure and temperature and the chemical compositions of all the phases present. Since the value of the free energy function is a minimum when the system is at equilibrium, this free energy function can then be minimized with respect to the chemical compositions of all phases, keeping P and T constant, subject to the conservation of mass constraints.

The total Gibb's free energy of a system at constant T and P is given by

$$G = \sum_i u_i n_i \qquad \text{(constant T, P)} \qquad (9)$$

where u_i is the chemical potential of chemical species i

n_i is the number of moles of chemical species i

The total number of moles of each element must be constant without regard to the distribution of the elements between the chemical compounds in the system. That is, the variations of the mole numbers n_i (δn_i) must satisfy the constraints of conservation of elements. These constraints may be written as follows:

$$\sum_{i=1}^{m} c_{ji} n_i - d_j = 0 \qquad j = 1,\ldots,l \qquad (10)$$

where m is the total number of chemical species in the system

c_{ji} is the number of atoms of element j in compound i

d_j is the total number of atoms of element j in the system

l is the total number of chemical elements in the system

As well, the mole numbers cannot be negative, that is:

$$n_i \geq 0 \qquad i=1,\ldots,m \qquad (11)$$

The chemical potential of component i is given by:

$$\mu_i = \mu_i^o + RT \ln \left(P\hat{\phi}_i \frac{ni}{Np}\right) \qquad (12)$$

where μ_i^o is the reference state chemical potential

R is the universal gas constant

$\hat{\phi}_i$ is the mixture fugacity coefficient

Np is the total number of moles in the phase where species i is found

The reference state can be chosen such that:

$$\mu_i^o = (\Delta G_f^o)_i$$

where $(\Delta G_f^o)_i$ is the standard Gibb's free energy of formation of gaseous i at a temperature T

The mixture fugacity coefficient is calculated using equation (8) and mixing rules for the R-K equation.

Traditionally, chemical systems were studied by defining stoichiometric equations based on the proposed reactions occurring and their associated equilibrium constants. The equilibrium product distribution was calculated by solving this set of non-linear equations. This method had certain drawbacks, the main one being that all reactions occurring had to be defined. Minimization of the system's free energy is considered more powerful.

3.2 Solution by Optimization - The SUMT Method

3.2.1 Formulation of the Problem

Given a non-linear function G consisting of known constants and N variables in Real Space $n_1, n_2, \ldots, n_N$ which are subject to equality and/or inequality constraints. The problem of finding the minimum of G, called the objective function, can be written as follows:

$$\min G(X) \qquad X = (n_1, n_2, \ldots, n_N)$$

with constraint functions

$$F_i(X) \geq 0 \qquad 0 < i \leq NCI$$

$$H_j(X) = 0 \qquad 0 < j \leq NCE$$

where NCI is the number of inequality constraints

and NCE is the number of equality constraints

When there are no constraints, that is when NCI and NCE are both zero, the problem is called a free minimization problem.

This problem, applied to minimization of Gibb's free energy of the system (G), can be written as:

$$\min G(X) \qquad X = (n_1, n_2, \ldots, n_N)$$

with constraint functions

$$F_i(X) \equiv n_i \geq 0 \qquad i = 1, \ldots, N$$

$$H_j(X) \equiv \sum_{i=1}^{n} c_{ji} n_i - d_j = 0 \qquad j = 1, \ldots, l$$

In this case, NCI = N and NCE = 1.

3.2.2 Transformation to Free Minimization

Free minimization problems are easily solved by various known techniques. However, a problem with constraints must be transformed to a free minimization problem or to a set of free minimization sub-problems. The method used for this transformation was the "Sequential Unconstrained Minimization Technique" (SUMT). The theoretical foundations of this method, developed by Fiacco and McCormick (1966), are summarized as follows.

If the functions G, F_i and H_i satisfy certain conditions of continuity, the equivalence of the following two problems (I) and (II) can be proven:

(I) $\min F(X)$

$G_i(X) \geq 0 \qquad 0 < i \leq NCI$

$H_j(X) = 0 \qquad 0 < j \leq NCE$

(II) $\min FOBJ(X, R_k)$ with $R_k \longrightarrow 0$

A properly defined physical problem will always satisfy the continuity conditions.

FOBJ, called the penalty function, is a combination of G, F_i and H_j into one function. The SUMT consists in sequentially solving a set of free minimization sub-problems (II) by giving R_k successively smaller values.

The general algorithm of the SUMT method is outlined as follows:

(a) Choose initial values of the variables $(n_1^o,\ldots,n_n^o,Ro)$. These may have any value except Ro which must be a positive number. The number of the iteration is k (initially, k = 1).

(b) From the values of the n_i^{k-1}, find the minimum point $(n_1^k,\ldots,n_n^k)$ of the function $FOBJ(n_1,\ldots,n_n,R_k)$ using a minimization technique.

(c) Determine if the n_i^k can be considered as the solution that is if FOBJ ≈ G; if not, go to step d.

(d) Choose R_{k+1} such that $0 < R_{k+1} < R_k$; set k=k+1 and return to step b.

3.2.3 Free Minimization Techniques

Free minimization methods are divided into two categories: (a) direct methods which require the iterative estimates of the penalty function Q to find the minimum; (b) descent methods which base themselves on the gradient of Q to determine directions of descent toward the minimum. Descent methods which utilize both first and second derivatives converge most rapidly to the solution. A detailed description of minimization techniques, including convergence criteria has been published by Jacoby et al., (1972).

For this study, a descent method was used called Newton's method with descent steps, improved by de Broissia and Lemieux (1976) and utilizing first and second derivatives of the objective function. This type is the most efficient of the minimization techniques. One of the advantages of using the method of de Broissia and Lemieux is that the initial values chosen for the variables of the objective function do not greatly affect final convergence to the solution. The initial point does not even have to satisfy the constraints.

The initial value of r used most frequently is $r^o = 1.0$. However, the method allows calculation of r^o using theoretical formulae.

Each time a minimum is determined, the value of r must be reduced so that $0 < r^{k+1} < r$. The following recursive formula was used:

$$r^{k+1} = r^k/C$$

where $4 \leq C \leq 16$

Experience has shown that generally, the best value for C is 4.

3.3 Limitations of the Method

The most serious source of error in this method is associated with the mixing rules of the R-K equation. To obtain reliable results for phase compositions it is necessary to include the Θ_{ij} parameters (Hirata et al., 1975). Unfortunately, these quantities are temperature dependent and, to our knowledge, no means for correcting them has yet been devised. As well, calculations done during this project suggested that these constants can be somewhat pressure dependent. Therefore, more work is required to study the properties and suitability of the R-K equation in greater detail.

The general consensus is that the method works well only for non-polar, non hydrogen bonding molecules. A specific criticism of the R-K equation is that predicted liquid molar volumes are often not equal to experimental molar volumes (Horvath, 1972). However, this did not apply to the present application, since the R-K parameters were adjusted so the calculated molar volume of the liquid would be correct. This procedure may also have helped to alleviate any problem caused by the presence of polar and hydrogen bonding molecules in the system.

4.0 RESULTS

4.1 Literature Review

Considering the semi-empirical nature of the R-K and Wilson equations, a large body of experimental data is required to obtain the necessary parameters used in equations of state. Therefore, a literature review on the thermodynamics of chemical systems in equilibrium was completed.

Our efforts were concentrated on material published after 1965 since, before this date, few non-ideal systems had been studied. More than 150 articles were found and classified into two groups: publications dealing with the theory of vapour-liquid and chemical equilibria and those dealing with experimental data on chemical systems in equilibrium. Authors, titles and sources were tabulated in a reference guide, included as Appendix 3.

A complete summary of the data found in these articles is beyond the scope of this project. However, a good compilation of data required for equations of state can be found in a book authored by Hirata et al., (1975). Binary mixture data for a variety of liquid-liquid and liquid-gas systems were tabulated and then correlated using either the Wilson equation or the Redlich-Kwong equation.

The apparent emphasis in the literature is on light hydrocarbons, which reflects the fact that most vapour-liquid equilibria data are derived from studies relevant to the petroleum industry. Recently, however, the increased interest in coal gasification and liquefaction has resulted in the publication of vapour-liquid equilibria data on binary, ternary, or multicomponent systems of importance to these processes.

Of particular interest to this project was a paper on the phase equilibrium of gaseous hydrogen in tetralin at operating conditions of interest for coal liquefaction processes (Simnick et al., 1977). The purpose of the study was to obtain information on the amount of dissolved hydrogen in the liquid phase, which would be useful for analysis of reaction mechanisms and for engineering design of blowdown and associated separation systems. Equilibrium saturated liquid and gas compositions were determined at four temperatures and seven pressures ranging from 462.7 K to 662.2 K and 2.03 MPa to 25.3 MPa respectively.

4.2 Mass Balance

To obtain the mass balance constraints represented by equation (10), the constants d_j were calculated using the elemental composition of ash free lignite (reported in Chapter 2) and three CO/H_2 ratios. The results of these calculations are given in Table 55.

The values c_{ji} (number of atoms of element j in compound i) depend on the chemical species present in the equilibrium mixture. For example, if compound #3 was phenol (C_6H_6O), the c_{ji} pertaining to this product would have the following values:

$c_{13} = 6$ (for element 1, carbon)

$c_{23} = 6$ (for element 2, hydrogen)

$c_{33} = 1$ (for element 3, oxygen)

4.3 Products

Initially, the species chosen to be present were solid carbon (C_s), hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O), methane (CH_4), benzene (C_6H_6) and tetralin ($C_{10}H_{12}$). This small data base, used to test the procedure, was eventually extended to include phenol (C_6H_6O), cyclohexanol ($C_6H_{12}O$), benzoic acid ($C_7H_6O_2$), naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$).

The computer programme developed for this method functioned well for operating conditions where a gas phase was predicted. However, when only a liquid phase was predicted, the mole number of all gaseous components tended to zero. This created a non-equilibrium situation which caused the computations to diverge. At most of the operating conditions considered (600 K to 750 K and 15 MPa to 30 MPa), the programme predicted principally a liquid phase which dissolved the gas phase. When this project was completed, the divergence problem had unfortunately not been solved. Therefore, no results were available pertaining to the effect of operating conditions on equilibrium composition.

The solution to this problem was close at hand. We believe that when conditions favoured a vanishing gas phase, the largest root of molar volume in the R-K equation became complex. This would result in erroneous values for the derivatives of the free energy function. Since the optimization routine is dependent on these derivatives, errors in their computation would cause divergence. This problem may be solved by modifying the computer programme so that when a vanishing

Table 55: Total number of atoms of each element in the system[1]

CO/H_2 Molar Ratio	d_1 (for element carbon)	d_2 (for element hydrogen)	d_3 (for element oxygen)
0.33/1	9.24	20.96	8.07
1/1	15.94	20.96	14.77
3/1	35.94	20.96	34.77

[1] basis is 100 g of ash-free lignite with the elemental composition given in Chapter 2, and 10 moles of H_2.

gas phase is encountered, the computations are restarted without consideration to gaseous components. Time constraints prevented the testing of this modification.

A copy of the existing computer programme and a user's guide are included as appendices 4 and 5.

4.4 Future Work

Work on the thermodynamics of coal liquefaction should be continued. The tasks involved should include the following:

(a) modification of the existing computer programme to allow prediction of the components when only a liquid phase exists;

(b) improvement of a thermodynamic data base for coal liquefaction products;

(c) investigation of solid-liquid equilibria;

(d) adaptation to a kinetic model.

Continuation of this work is justified since the initial computer programme development work is already completed. The fact that a liquid oil phase was predicted to predominate is an encouraging result of our preliminary investigations. As well, results of other workers have shown that yields from liquefaction are constrained by thermodynamic properties (see Chapter 1, p. 26). In the least, the development of this method would allow prediction of the quantity of gas dissolved in and the phase structure of a reacting mixture. This should aid engineering design and kinetic modelling of coal liquefaction.

CONCLUSIONS

Past Work on Coal Hydrogenolysis

Based on a literature overview, the following conclusions may be drawn:

1. Present day developments in coal liquefaction originate from early German processes developed by Bergius and Fisher-Tropsch.

2. No clear relationships exist between coal composition and liquid oil yields from hydrogenolysis. Properties such as elemental composition, rank and petrographic composition affect conversions and product yields in a complex fashion not yet understood.

3. Solvents having hydrogen donor and transfer properties are essential in directing hydrogenolysis to liquids rather than gases and solids.

4. Added catalysts do not increase conversion of or oil yields from low rank coals.

5. The best catalysts for hydrorefining and hydrocracking of oils produced from liquefaction are metal sulphides and oxides.

6. Most liquefaction processes produce synthetic crude oil or solvent refined coal as well as other fuel by products such as naphtha and synthesis gas.

7. All hydrogenolysis processes require a coal gasification step to produce either hydrogen or synthesis gas.

Experimental Hydrogenolysis of Lignite

The following conclusions may be drawn regarding lignite liquefaction at operating conditions used during this study:

1. Lignite is hydrogenolysed very rapidly, within the first few minutes at the reaction temperature, but further hydrogenation of liquid products occurs much slower.

2. Competition between coke formation, liquid formation and gasification during liquefaction is highly sensitive to temperature changes but less to pressure and residence time.

3. Increasing residence time tends to increase coal solubilization, thereby improving liquid yields.

4. Maximum liquid yields are obtained by lowering temperature, and increasing pressure and carbon monoxide content in the gas phase.

5. However, higher temperatures favour deoxygenation of the oil products.

6. Increasing reaction temperature increases conversion but favours gasification rather than liquid formation.

7. The addition of catalysts (cobalt molybdate on alumina; nickel or iron on peat char) does not substantially affect lignite conversions or liquid oil yields, but increases the light oil fraction.

8. Secondary catalytic treatment of the liquid oil product does not seem to increase its hydrogen content.

9. The CO/H_2 ratio is not constant during a batch reaction since the heating rate affects the reactivity of gases.

10. No significant conclusions can be drawn regarding desulphurization, denitrification and catalytic deoxygenation. The lignite used already had low sulphur and nitrogen contents, and air contact during product upgrading and storage increased the oxygen content of the liquid oil.

Equilibrium Thermodynamics

1. Thermodynamic models based on ideal behavior are inadequate for liquefaction processes.

2. An extension of methods used to solve non-ideal vapour-liquid equilibria is probably the most promising approach to a study of complex chemical equilibria.

3. Of the two phase equilibria equations considered, the Redlich-Kwong equation of state seemed easier to use since both gases and liquids are postulated to have the same reference state.

4. A large quantity of vapour-liquid equilibria data are available, but the emphasis is on light hydrocarbons at conditions relevant to the petroleum industry.

5. At operating conditions used for coal liquefaction, the model predicted the principal phase to be a liquid.

6. Additional work is required to allow prediction of liquid phase concentrations when the gas phase vanishes.

RECOMMENDATIONS

Further work should be conducted on lignite liquefaction. The following are tasks recommended for consideration:

1. Catalytic screening experiments should be conducted to increase the hydrogen/carbon ratio and decrease the oxygen, sulphur and nitrogen content in liquid oil products, and to lower operating conditions while maintaining product quantity and quality.

2. Care should be taken during future work to avoid contacting the oil products with air in order to determine their true oxygen content.

3. The solubility and adsorption of oxygen in the liquid oil products should be determined.

4. Screening experiments with a high sulphur lignite should be conducted to determine the desulphurization ability of the ash fraction in the coal.

5. Short residence time kinetic studies should be conducted to gain insight into factors affecting reactivity and selectivity.

6. A study on the fundamental role of minerals present in coal ash should be conducted which would include state of the metal constituents (chelate, ligand, inorganic salt), types of reactions catalyzed by coal ash constituents, and effect of sulphur and nitrogen on catalytic activity.

7. This study should be extended to hydrogenolysis of peat and coal tar.

8. Development of the thermodynamic model described in this report should be continued.

9. The thermodynamic data base for coal liquefaction products should be increased by conducting vapour-liquid equilibria studies.

10. Eventually, continuous flow liquefaction of lignite should be conducted to obtain an economic assessment of the process.

11. The hydrocracking and hydrorefining behavior of the liquid oil products should be studied.

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APPENDIX 1

SUMMARY OF WORK PROPOSED FOR PHASE 2

A summary of the work proposed for Phase 2 of this project is presented in this appendix. The following tasks were proposed, in consultation with the Scientific Authority from Energy, Mines and Resources Canada:

Production of Concentrated Recycle Oil

Five batch liquefaction experiments will be conducted to produce a concentrated recycle oil. Approximately 100 g of lignite (as received) will be mixed with 100 g of anthracene oil and the mixture hydrogenolyzed at conditions found optimum in Phase 1. All the liquid oil product obtained will be mixed with another 100 g fraction of lignite and the mixture hydrogenolyzed at optimum conditions. This process will be repeated three times to obtain a final liquid product more concentrated in recycle oil than anthracene oil.

The final concentrated recycle oil will be analyzed for elemental C, H, O, N and S, ash content, fixed carbon and the following metals: Al, Co, Cu, Fe, K, Li, Mn, Mo, Na, Ni, Sn, V.

Catalytic Upgrading of Liquid Products

Approximately twelve (12) catalytic liquefaction experiments will be conducted to upgrade liquid products while lowering the severity of operating conditions.

The catalysts tested will be presulphided cobalt-molybdate and nickel-molybdate on alumina. Standard commercial and/or specially prepared catalysts will be used.

Hydrogenolysis will be carried out using carbon monoxide-hydrogen mixtures and moderate operating conditions (3500 kPa - 10,000 kPa; 450 K - 650 K). The CO/H_2 ratio and gaseous hydrocarbon composition will be monitored with a gas chromatograph. Liquid oil products will be analyzed for elemental C, H, O, N and S, ash content and fixed carbon. As well, the residues will be analyzed for elemental C, H, O, N and S and the metals Al, Co, Cu, Fe, K, Li, Mn, Mo, Na, Ni, Sn and V.

A number of the liquid products will be distilled into five fractions to determine their boiling point distribution.

The catalytic and operating conditions producing an optimum quality and quantity of product will be determined. Comparative experiments will be conducted at these conditions using the concentrated recycle oil produced during the first task.

This task should provide an indication of the feasibility of reducing oxygen, nitrogen and sulphur contents in liquid oil products, when using both anthracene oil as solvent or concentrated recycle oil.

Liquefaction of North Dakota Lignite

Approximately four liquefaction experiments will be conducted using lignite obtained from the Indianhead Mine, Zap, North Dakota. The purpose of this task is to compare the results obtained during this project using a Saskatchewan lignite with the results obtained by a group at the University of North Dakota using the Zap lignite.

The non-filterable products will be extracted with benzene followed by a pyridine extraction, since this latter compound is the extractant employed by the North Dakota group.

The liquefaction products will be fractionated into five cuts. As well, all products obtained will be chemically characterized as in the previous task.

Modification of the Apparatus

The experimental work conducted during Phase 1 indicated that certain modifications to the existing equipment would be required to better control the liquefaction process and to obtain more precise results. Specifically, the modifications would attempt the following: facilitate separation of liquid from solid products; minimize air contact with hot liquid products; sample the liquid phase during the reaction; continuously monitor the gas phase; control more easily the carbon monoxide/hydrogen ratio in the reacting mixture as well as process pressure.

An extra sampling tube will be inserted into the existing autoclave and connected to an enclosed filter apparatus. The autoclave will also be connected to a compressor and a system of regulators and valves to allow continuous flow of the gas phase.

Catalytic Liquefaction of Saskatchewan Lignite

Following equipment modifications, approximately forty (40) catalytic liquefaction experiments will be conducted. The objectives of this task include increasing the hydrogen/carbon ratio in the liquid oil products, decreasing the oxygen, nitrogen and sulphur content in the liquid oil products, and lowering operating conditions (temperature and pressure) while maintaining product quality and quantity.

The following catalytic systems may be tested:

- supported cobalt-molybdenum catalysts on alumina containing alkali promoters which were developed at CANMET's Energy Research Laboratories
- metal catalysts supported on peat char, developed at the University of Sherbrooke
- recycled ash obtained by oxidation of the organic fraction in the unextracted residue produced during liquefaction
- recycled ash impregnated with alkali or other metals
- inexpensive ore tailings obtained from various mining operations.

The final choice of catalysts and operating conditions will be done in conjunction with the Scientific Authority.

Recovery and regeneration of the cobalt-molybdenum catalysts will be attempted. Approximately 25% of the liquid products will be fractionated into their significant cuts. All products will be chemically characterized as in previous tasks.

Theoretical Aspects of Coal Liquefaction

In consultation with the Scientific Authority, various theoretical aspects of coal conversion will be studied. The work conducted during this phase may include the following:

- development of a kinetic model using gas and liquid sampling data, possibly as well as hign performance liquid chromatography data
- postulation of rate constants and mechanisms associated with coal hydrogenolysis
- improvement of the thermodynamic model for coal liquefaction developed in Phase 1
- development of a thermodynamic data base for coal liquefaction products
- comparison of thermodynamic data with experimental and kinetic data
- modelling of liquid phase heat capacities

Literature Review

During the project, the published literature will be periodically searched to obtain the latest developments in this field of study.

A state of the art review will be conducted to determine previous uses of homogeneous catalysts during coal conversion and patents obtained in coal liquefaction. Relevant papers will be collected and their contents summarized.

APPENDIX 2

VARIATION OF GAS COMPOSITION WITH REACTION TIME

This appendix presents the gas phase compositions during the hydrogenolysis reaction for each experiment. The times shown refer to the time after the chemical mixture reached the reaction temperature. Compositions are given in molar percentages.

TABLE A1: GAS PHASE COMPOSITION - EXPERIMENT NO. 1

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	5 minutes	10 minutes		
HYDROGEN	64.93	70.47	71.89		
CARBON MONOXIDE	30.59	23.34	21.09		
CARBON DIOXIDE	4.48	5.99	6.29		
METHANE	-	-	0.14		
C_2 HYDROCARBONS	-	0.06	0.39		
C_4 HYDROCARBONS	-	0.14	0.20		

reaction temperature (K): 653
initial CO/H_2 molar ratio: 0.33/1
initial pressure (MPa): 7.1
residence time at reaction temperature (minutes): 10

TABLE A2 : GAS PHASE COMPOSITION - EXPERIMENT NO. 2

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	5 minutes	10 minutes		
HYDROGEN	69.70	66.34	68.52		
CARBON MONOXIDE	22.73	18.35	16.28		
CARBON DIOXIDE	6.34	11.92	9.91		
METHANE	0.55	2.11	3.25		
C_2 HYDROCARBONS	0.37	0.77	1.24		
C_3 HYDROCARBONS	0.27	0.35	0.57		
C_4 HYDROCARBONS	0.04	0.16	0.23		

reaction temperature (K): 733
initial CO/H_2 molar ratio: 0.33/1
initial pressure (MPa): 7.1
residence time at reaction temperature (minutes): 10

TABLE A3 : GAS PHASE COMPOSITION - EXPERIMENT NO. 3

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	5 minutes	10 minutes		
HYDROGEN	22.86		32.03		
CARBON MONOXIDE	72.01		53.33		
CARBON DIOXIDE	4.50		14.04		
METHANE	-		0.23		
C_2 HYDROCARBONS	-		0.13		
C_3 HYDROCARBONS	-		0.03		
C_4 HYDROCARBONS	-		0.07		
> C_4 HYDROCARBONS	-		0.07		
AMMONIA	0.13		0.07		

reaction temperature (K): 653
initial CO/H_2 molar ratio: 3/1
initial pressure (MPa): 7.1
residence time at reaction temperature (minutes): 10

TABLE A4: GAS PHASE COMPOSITION - EXPERIMENT NO. 4

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	5 minutes	10 minutes		
HYDROGEN	21.85	40.07	26.73		
CARBON MONOXIDE	61.48	17.37	48.47		
CARBON DIOXIDE	15.89	33.99	20.92		
METHANE	0.59	5.03	2.38		
C_2 HYDROCARBONS	0.17	1.90	0.86		
C_3 HYDROCARBONS	0.08	0.93	0.38		
C_4 HYDROCARBONS	-	0.33	0.15		
> C_4 HYDROCARBONS	-	-	0.11		
AMMONIA	-	0.38	-		

reaction temperature (K): 733
initial CO/H_2 molar ratio: 3/1
initial pressure (MPa): 7.1
residence time at reaction temperature (minutes): 10

TABLE A5: GAS PHASE COMPOSITION - EXPERIMENT NO. 5.

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	5 minutes	10 minutes		
HYDROGEN	59.39	63.95	71.60		
CARBON MONOXIDE	38.38	30.43	23.50		
CARBON DIOXIDE	2.28	5.62	4.81		
C_2 HYDROCARBONS	-	-	0.06		
C_4 HYDROCARBONS	-	-	0.03		

reaction temperature (K): 653
initial CO/H_2 molar ratio: 0.33/1
initial pressure (MPa): 11.1
residence time at reaction temperature (minutes): 10

TABLE A6 : GAS PHASE COMPOSITION - EXPERIMENT NO. 6

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	5 minutes	10 minutes		
HYDROGEN	77.31	55.28	71.27		
CARBON MONOXIDE	13.07	28.96	19.65		
CARBON DIOXIDE	8.55	11.56	6.05		
METHANE	-	3.52	1.75		
C_2 HYDROCARBONS	0.52	-	0.67		
C_3 HYDROCARBONS	-	-	0.40		
C_4 HYDROCARBONS	0.55	0.68	0.13		
AMMONIA	-	-	0.08		

reaction temperature (K): 733
initial CO/H_2 molar ratio: 0.33/1
initial pressure (MPa): 11.1
residence time at reaction temperature (minutes): 10

TABLE A7 : GAS PHASE COMPOSITION - EXPERIMENT NO. 7

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	5 minutes	10 minutes		
HYDROGEN	25.83	10.99	23.62		
CARBON MONOXIDE	67.89	83.37	65.32		
CARBON DIOXIDE	5.91	5.49	10.45		
METHANE	-	-	0.38		
C_2 HYDROCARBONS	-	-	0.04		
AMMONIA	0.37	0.15	0.19		

reaction temperature (K): 653
initial CO/H_2 molar ratio: 3/1
initial pressure (MPa): 11.1
residence time at reaction temperature (minutes): 10

TABLE A8 : GAS PHASE COMPOSITION - EXPERIMENT NO. 8

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	5 minutes	10 minutes		
HYDROGEN	23.91	30.56	26.49		
CARBON MONOXIDE	64.97	65.78	61.19		
CARBON DIOXIDE	10.01	1.08	9.44		
METHANE	0.46	1.70	1.89		
C_2 HYDROCARBONS	0.21	-	0.56		
C_3 HYDROCARBONS	0.21	-	0.22		
C_4 HYDROCARBONS	-	0.28	0.04		
$>C_4$ HYDROCARBONS	-	0.23	0.05		
AMMONIA	0.23	0.37	0.12		

reaction temperature (K): 733
initial CO/H_2 molar ratio: 3/1
initial pressure (MPa): 11.1
residence time at reaction temperature (minutes): 10

TABLE A9 : GAS PHASE COMPOSITION - EXPERIMENT NO. 9

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	25 minutes	33 minutes	50 minutes	
HYDROGEN	79.90	70.06	67.39	50.02	
CARBON MONOXIDE	19.89	22.08	29.34	20.12	
CARBON DIOXIDE	0.12	7.07	5.04	20.37	
METHANE	-	0.51	0.87	6.26	
C_2 HYDROCARBONS	-	0.14	0.12	1.20	
C_3 HYDROCARBONS	-	0.05	0.05	1.20	
C_4 HYDROCARBONS	-	-	0.02	0.60	
$>C_4$ HYDROCARBONS	-	-	-	0.20	
AMMONIA	0.09	0.09	0.14	0.03	

reaction temperature (K): 653
initial CO/H_2 molar ratio: 0.33/1
initial pressure (MPa): 7.1
residence time at reaction temperature (minutes): 50

TABLE A10: GAS PHASE COMPOSITION - EXPERIMENT NO. 10

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	25 minutes	50 minutes		
HYDROGEN	68.58	60.06	55.94		
CARBON MONOXIDE	22.78	18.41	12.36		
CARBON DIOXIDE	7.32	15.29	21.36		
METHANE	0.74	4.14	6.26		
C_2 HYDROCARBONS	0.26	1.32	1.87		
C_3 HYDROCARBONS	0.05	0.48	1.27		
C_4 HYDROCARBONS	0.03	0.11	0.62		
> C_4 HYDROCARBONS	0.10	-	0.29		
AMMONIA	0.14	0.19	0.03		

reaction temperature (K): 733
initial CO/H_2 molar ratio: 0.33/1
initial pressure (MPa): 7.1
residence time at reaction temperature (minutes): 50

TABLE A11: GAS PHASE COMPOSITION - EXPERIMENT NO. 11

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	25 minutes	50 minutes		
HYDROGEN	21.27	27.89	24.39		
CARBON MONOXIDE	75.12	55.92	56.58		
CARBON DIOXIDE	3.61	15.28	17.62		
METHANE	-	0.26	0.60		
C_2 HYDROCARBONS	-	0.12	0.23		
C_3 HYDROCARBONS	-	0.05	0.10		
C_4 HYDROCARBONS	-	0.04	0.10		
> C_4 HYDROCARBONS	-	-	0.08		
AMMONIA	-	0.44	0.30		

reaction temperature (K): 653
initial CO/H_2 molar ratio: 3/1
initial pressure (MPa): 7.1
residence time at reaction temperature (minutes): 50

TABLE A12: GAS PHASE COMPOSITION - EXPERIMENT NO. 12

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	25 minutes	50 minutes		
HYDROGEN	24 .78	45.93	22.85		
CARBON MONOXIDE	61.83	19.58	29.89		
CARBON DIOXIDE	12.50	17.18	37.91		
METHANE	0.13	10.29	5.54		
C_2 HYDROCARBONS	0.37	3.40	1.87		
C_3 HYDROCARBONS	0.39	1.30	0.91		
C_4 HYDROCARBONS	-	0.76	0.51		
> C_4 HYDROCARBONS	-	0.50	0.54		
AMMONIA	-	1.05	-		

reaction temperature (K): 733
initial CO/H_2 molar ratio: 3/1
initial pressure (MPa): 7.1
residence time at reaction temperature (minutes): 50

TABLE A13: GAS PHASE COMPOSITION - EXPERIMENT NO. 13

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	25 minutes	35 minutes	40 minutes	50 minutes
HYDROGEN	73.47	71.69	65.49	67.34	63.93
CARBON MONOXIDE	24.28	20.92	23.07	19.93	21.02
CARBON DIOXIDE	2.25	6.79	11.02	11.51	14.02
METHANE	-	0.43	-	0.77	0.51
C_2 HYDROCARBONS	-	0.10	0.12	0.25	0.31
C_3 HYDROCARBONS	-	0.07	-	0.03	0.13
C_4 HYDROCARBONS	-	-	0.30	0.03	0.08
> C_4 HYDROCARBONS	-	-	-	0.14	-

reaction temperature (K): 653
initial CO/H_2 molar ratio: 0.33/1
initial pressure (MPa): 11.1
residence time at reaction temperature (minutes): 50

TABLE A14: GAS PHASE COMPOSITION - EXPERIMENT NO. 14

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	25 minutes	30 minutes	40 minutes	50 minutes
HYDROGEN	66.30	67.90	65.48	74.49	57.70
CARBON MONOXIDE	26.72	18.34	12.83	15.68	23.27
CARBON DIOXIDE	5.84	8.51	15.29	1.54	8.20
METHANE	0.76	3.80	3.51	4.64	6.70
C_2 HYDROCARBONS	0.38	0.84	1.44	1.75	1.73
C_3 HYDROCARBONS	-	0.44	0.74	0.88	1.04
C_4 HYDROCARBONS	-	0.09	0.42	0.47	0.79
> C_4 HYDROCARBONS	-	0.08	0.28	0.55	0.60

reaction temperature (K): 733
initial CO/H_2 molar ratio: 0.33/1
initial pressure (MPa): 11.1
residence time at reaction temperature (minutes): 50

TABLE A15: GAS PHASE COMPOSITION - EXPERIMENT NO. 15

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	25 minutes	30 minutes	50 minutes	
HYDROGEN	23.12	24.66	22.84	23.32	
CARBON MONOXIDE	73.85	67.09	62.15	57.56	
CARBON DIOXIDE	2.58	8.09	14.73	18.20	
METHANE	-	-	-	0.43	
C_2 HYDROCARBONS	-	0.03	0.08	0.15	
C_3 HYDROCARBONS	-	-	0.06	0.03	
C_4 HYDROCARBONS	0.12	-	-	0.03	
> C_4 HYDROCARBONS	0.10	0.13	0.14	0.13	
AMMONIA	0.23	-	-	0.15	

reaction temperature (K): 653
initial CO/H_2 molar ratio: 3/1
initial pressure (MPa): 11.1
residence time at reaction temperature (minutes): 50

TABLE A16: GAS PHASE COMPOSITION - EXPERIMENT NO. 16

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	25 minutes	30 minutes	40 minutes	50 minutes
HYDROGEN	20.49	21.06	19.76	20.60	21.56
CARBON MONOXIDE	67.90	59.03	55.33	47.54	44.87
CARBON DIOXIDE	10.83	17.79	20.64	26.25	28.67
METHANE	-	0.26	1.98	3.00	2.68
C_2 HYDROCARBONS	0.18	0.59	0.88	0.90	0.95
C_3 HYDROCARBONS	0.33	0.54	0.48	0.57	0.50
C_4 HYDROCARBONS	-	0.49	0.31	0.34	0.19
> C_4 HYDROCARBONS	0.19	0.24	0.34	0.51	0.28
AMMONIA	0.08	-	0.28	0.29	0.30

reaction temperature (K): 733
initial CO/H_2 molar ratio: 3/1
initial pressure (MPa): 11.1
residence time at reaction temperature (minutes): 50

TABLE A17: GAS PHASE COMPOSITION - EXPERIMENT NO. 17

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	15 minutes	30 minutes		
HYDROGEN	50.35	47.22	40.97		
CARBON MONOXIDE	43.44	39.23	35.73		
CARBON DIOXIDE	5.48	11.71	19.95		
METHANE	0.37	0.96	1.59		
C_2 HYDROCARBONS	-	0.40	0.52		
C_3 HYDROCARBONS	-	0.17	0.26		
C_4 HYDROCARBONS	-	0.20	0.16		
> C_4 HYDROCARBONS	-	-	0.20		
AMMONIA	0.36	0.11	0.62		

reaction temperature (K): 693
initial CO/H_2 molar ratio: 1/1
initial pressure (MPa): 9.1
residence time at reaction temperature (minutes): 30

TABLE A18: GAS PHASE COMPOSITION - EXPERIMENT NO. 18

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	15 minutes	30 minutes		
HYDROGEN	45.52	43.20	46.13		
CARBON MONOXIDE	47.23	45.12	33.29		
CARBON DIOXIDE	6.43	9.83	18.44		
METHANE	0.08	0.96	0.92		
C_2 HYDROCARBONS	0.46	0.35	0.53		
C_3 HYDROCARBONS	-	0.15	0.16		
C_4 HYDROCARBONS	-	0.08	0.11		
> C_4 HYDROCARBONS	-	0.14	0.16		
AMMONIA	0.28	0.17	0.26		

reaction temperature (K): 693
initial CO/H_2 molar ratio: 1/1
initial pressure (MPa): 9.1
residence time at reaction temperature (minutes): 30

TABLE A19: GAS PHASE COMPOSITION - EXPERIMENT NO. 19

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	15 minutes	30 minutes		
HYDROGEN	48.49	48.40	46.90		
CARBON MONOXIDE	46.53	37.15	31.41		
CARBON DIOXIDE	4.37	13.23	18.46		
METHANE	0.13	0.41	1.07		
C_2 HYDROCARBONS	0.04	0.33	0.72		
C_3 HYDROCARBONS	-	0.21	0.39		
C_4 HYDROCARBONS	-	0.11	0.27		
> C_4 HYDROCARBONS	-	-	0.39		
AMMONIA	0.44	0.16	0.39		

reaction temperature (K): 693
initial CO/H_2 molar ratio: 1/1
initial pressure (MPa): 9.1
residence time at reaction temperature (minutes): 30

TABLE A20: GAS PHASE COMPOSITION - EXPERIMENT NO. 20

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	30 minutes			
HYDROGEN	37.60	45.35			
CARBON MONOXIDE	53.88	31.99			
CARBON DIOXIDE	7.13	16.21			
METHANE	0.30	1.03			
C_2 HYDROCARBONS	0.04	0.32			
UNIDENTIFIED	1.05	5.10			

catalyst/lignite (maf) weight ratio:	0.163 MB306/1
reaction temperature (K):	693
initial CO/H_2 molar ratio:	1/1
initial pressure (MPa):	9.1
residence time at reaction temperature (minutes):	30

TABLE A21: GAS PHASE COMPOSITION - EXPERIMENT NO. 21

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	15 minutes	30 minutes		
HYDROGEN	40.18	42.48	57.71		
CARBON MONOXIDE	52.55	30.26	20.74		
CARBON DIOXIDE	6.50	18.19	18.68		
METHANE	-	0.53	1.54		
C_2 HYDROCARBONS	-	0.40	0.37		
C_3 HYDROCARBONS	-	-	0.10		
> C_4 HYDROCARBONS	0.77	-	-		
UNIDENTIFIED	-	8.14	0.86		

catalyst/lignite (maf) weight ratio:	0.163 MB289/1
reaction temperature (K):	693
initial CO/H_2 molar ratio:	1/1
initial pressure (MPa):	9.1
residence time at reaction temperature (minutes):	30

TABLE A22: GAS PHASE COMPOSITION - EXPERIMENT NO. 22

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	15 minutes	30 minutes		
HYDROGEN	53.58	31.83	52.22		
CARBON MONOXIDE	39.82	44.80	27.33		
CARBON DIOXIDE	5.98	16.68	18.17		
METHANE	0.19	2.42	1.31		
C_2 HYDROCARBONS	0.08	0.71	0.12		
UNIDENTIFIED	0.35	3.56	0.85		

catalyst/lignite (maf) weight ratio:	0.140 Ni^{+2} on C/1
reaction temperature (K):	693
initial CO/H_2 molar ratio:	1/1
initial pressure (MPa):	9.1
residence time at reaction temperature (minutes):	30

TABLE A23: GAS PHASE COMPOSITION - EXPERIMENT NO. 23

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	15 minutes	30 minutes		
HYDROGEN	49.16	31.49	50.16		
CARBON MONOXIDE	42.42	40.46	29.39		
CARBON DIOXIDE	6.53	22.90	17.68		
METHANE	0.23	1.85	1.05		
C_2 HYDROCARBONS	0.06	0.63	0.51		
C_3 HYDROCARBONS	-	-	0.13		
UNIDENTIFIED	1.60	2.67	1.08		

catalyst/lignite (maf) weight ratio:	0.0496 Fe^{+3} on C/1
reaction temperature (K):	693
initial CO/H_2 molar ratio:	1/1
initial pressure (MPa):	9.1
residence time at reaction temperature (minutes):	30

TABLE A24: GAS PHASE COMPOSITION - EXPERIMENT NO. 24

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	15 minutes	30 minutes		
HYDROGEN	59.34	44.81	56.24		
CARBON MONOXIDE	39.65	50.56	40.90		
CARBON DIOXIDE	0.25	0.84	0.82		
METHANE	-	-	0.56		
C_2 HYDROCARBONS	-	0.10	0.11		
AMMONIA	-	0.88	0.36		
UNIDENTIFIED	0.77	2.81	1.00		

catalyst/oil weight ratio: 0.0467 MB306/1
reaction temperature (K): 693
initial CO/H_2 molar ratio: 1/1
initial pressure (MPa): 9.1
residence time at reaction temperature (minutes): 30

TABLE A25: GAS PHASE COMPOSITION - EXPERIMENT NO. 25

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	15 minutes	30 minutes		
HYDROGEN	45.10	35.05	51.63		
CARBON MONOXIDE	53.57	60.14	46.44		
CARBON DIOXIDE	0.33	0.73	0.86		
METHANE	-	-	0.30		
C_2 HYDROCARBONS	-	-	0.09		
> C_4 HYDROCARBONS	-	0.28	0.08		
AMMONIA	0.15	-	-		
UNIDENTIFIED	0.85	3.80	0.60		

catalyst/oil weight ratio:	0.0468 MB289/1
reaction temperature (K):	693
initial CO/H_2 molar ratio:	1/1
initial pressure (MPa):	9.1
residence time at reaction temperature (minutes):	30

TABLE A26: GAS PHASE COMPOSITION - EXPERIMENT NO. 26

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	15 minutes	30 minutes		
HYDROGEN	53.40	34.57	51.06		
CARBON MONOXIDE	45.88	61.73	46.99		
CARBON DIOXIDE	0.17	0.93	0.88		
METHANE	-	0.16	0.38		
C_2 HYDROCARBONS	-	0.08	-		
> C_4 HYDROCARBONS	0.05	-	0.11		
UNIDENTIFIED	0.50	2.53	0.58		

catalyst/oil weight ratio:	0.0412 Ni^{+2} on C/1
reaction temperature (K):	693
initial CO/H_2 molar ratio:	1/1
initial pressure (MPa):	9.1
residence time at reaction temperature (minutes):	30

TABLE A27: GAS PHASE COMPOSITION - EXPERIMENT NO. 27

CHEMICAL COMPONENT	TIME AT REACTION TEMPERATURES				
	0 minutes	15 minutes	30 minutes		
HYDROGEN	45.69	48.93	45.59		
CARBON MONOXIDE	53.79	46.89	52.15		
CARBON DIOXIDE	0.25	0.94	0.61		
METHANE	-	0.60	0.57		
C_2 HYDROCARBONS	-	0.14	0.16		
> C_4 HYDROCARBONS	-	0.18	0.17		
UNIDENTIFIED	0.27	2.32	0.76		

catalyst/oil weight ratio: 0.0196 Fe^{+3} on C/1
reaction temperature (K): 693
initial CO/H_2 molar ratio: 1/1
initial pressure (MPa): 9.1
residence time at reaction temperature (minutes): 30

APPENDIX 3

REFERENCES FOR DATA AND ESTIMATION TECHNIQUES ON VAPOUR-LIQUID EQUILIBRIA

Section 1: (continued)

Compound	References
Naphthalene	1
neopentane	43
Octane, n-	10, 18
octene, 1-	54
Pentafluoroethyl chloride	4
pentane, n-	28, 31, 39
propane	4, 28, 51
propylene	51
pyrene	52
pyridine	15
Tetralin	21, 47
toluene	31
triphenylene	52
Water	48
Xylene, o-	26
m-	26, 54
p-	26

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APPENDIX 4

LISTING OF THE OPTIMIZATION PROGRAM

This appendix is a listing of the computer programme and a typical output printout. The main programme is given first, followed by the subroutines in alphabetical order, and finally by the printout.

```
      PROGRAM TT(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
      REAL LAMBCA,M1,M,LAMD
      COMMON/DERIV/DEL2(25,25),DEL1(25),X(25),DER(25),N
      COMMON/CHCTX/INIT,IPOS
      COMMON/CONT/NCI,NCE,IPROB,IDER
      COMMON/ACC/R,INIT
      COMMON/FONCT/NFOBJ
      COMMON/ECRIT/IMPRIM
      DIMENSION S(25),DELX(25),B(25),C(25),XA(15,3)
      DIMENSION V(25)
      PRINT2016
      WRITE(6,8000)
 8000 FORMAT(5X,*PROGRAMME PARAMETERS*/)
      READ(5,*)N,NCI,NCE
      PRINT7741,N,NCI,NCE
 7741 FORMAT(1X,*N=*,I3,5X,*NCI=*,I3,3X,*NCE=*,I3)
      READ(5,*)(X(I),I=1,N)
      READ(5,*)IMET,IPOS,LECT,IMPRIM,IDER
      PRINT7742,IMET,IPOS,LECT,IMPRIM,IDER
 7742 FORMAT(1X,*IMET=*,I2,3X,*IPOS=*,I2,3X,*LECT=*,I2,3X,*IMPRIM=*,
     1      I2,1X,*IDER=*,I2)
      READ(5,*)IROPT,IGAIN,K1,IVER,KEX,IPROB
      PRINT7743,IROPT,IGAIN,K1,IVER,KEX,IPROB
 7743 FORMAT(1X,*IROPT=*,I2,2X,*IGAIN=*,I2,2X,*K1=*,I2,5X,*IVER=*,
     1      I2,3X,*KEX=*,I2,3X,*IPROB=*,I2)
      R=1.
      CA=4.
      NMAX=20
      NPMAX=3000
      IF(LECT.GT.1)READ(5,*)R,CA,NMAX,NPMAX
      PRINT7744,R,CA,NMAX,NPMAX
 7744 FORMAT(1X,*R=*,G10.3,3X,*CA=*,G10.3,2X,*NMAX=*,I3,2X,*NPMAX=*,
     1      I4)
      IFIN=1
      TAU1=1.E-5
      TAU2=1.E-5
      EPS1=1.E-6
      EPS2=1.E-10
      EPSF=1.E-6
      DIVE=1.E-6
      XLIM=1.E-6
      LAMD=1.
      LAMBCA=LAMD
      IF(LECT.EQ.2)READ(5,*)IFIN,TAU1,TAU2,EPS1,EPS2,EPSF,DIVE,XLIM
      PRINT7745,IFIN,TAU1,TAU2,EPS1,EPS2,EPSF,DIVE,XLIM
 7745 FORMAT(1X,*IFIN=*,I2/* TAU1=*,G15.7,5X,*TAU2=*,G15.7/
     1       1X,*EPS1=*,G15.7,5X,*EPS2=*,G15.7/
     1       1X,*EPSF=*,G15.7/
     1       1X,*DIVE=*,G15.7,5),*XLIM=*,G15.7)
      PRINT1002,(X(I),I=1,N)
 1002 FORMAT(/2X,*INITIAL ESTIMATES FROM 1 TO N*/9(2X,G12.5)
     1/9(2X,G12.5)//(2X,G12.5)/)
      ISF=1
      K=0
      IF=0
      II=0
```

```
                      TEST=0.
                      NFOBJ=0
 60                   INIT=0
                      IF(IMET.EQ.1)INIT=1
                8756  CALL ENTREE
                       CALL MODEL
                      PRINT2016
 65                   IF (IMPRIM.GT.0.AND.IVER-EQ.0) PRINT4473,ISP
                      IF (IMPRIM.GT.0.AND.IVER.EQ.0) PRINT510,9
                9999  CONTINUE
                600   L=K1
                      KX=1
 70             10    DERIVE=DIVE
                      DO 5 I=1,N
                      DER(I)=X(I)*DERIVE
                      IF(X(I).EQ.0.)DER(I)=DERIVE
                5     CONTINUE
 75                   IF(L.NE.K1) GO TO 12
                      ICC=0
                      L=0
                      CALL GRAD22,RETURNS(9999)
                      DO 555 I=1,N
 80                   DO 555 J=I,N
                555   DEL2(J,I)=DEL2(I,J)
                      IF(K.GT.0)GO TO 12
                      CALL FOBJ(M,N,X),RETURNS(9999,9999)
                C
 85             C
                C
                      IF(IVER-1)12,11,11
                11    CALL GRAD11,RETURNS(9999)
                      PRINT100
 90                   PRINT103,(DEL1(I),I=1,N)
                100   FORMAT(2X,*ANALYTICAL FIRST DEREIVATIVES, DEL(I),I=1,N*)
                101   FORMAT(2X,*ANALYTICAL SECOND DERIVATIVES,DEL(J,I),J=1,LINE*)
                103   FORMAT(2X,4G15.5)
                      CALL DIF1,RETURNS(9999)
 95                   PRINT104
                104   FORMAT(2X,*CENTRAL FINITE DIFFERENCES--FIRST DERIVATIVES*)
                      PRINT103,(DEL1(I),I=1,N)
                      PRINT101
                      DO 1000 J=1,N
100             1000  PRINT103,(DEL2(J,I),I=1,N)
                      PRINT111
                111   FORMAT(2X,*CENTRAL FINITE DIFFERENCES--SECOND DERIVATIVES*)
                      CALL DIF2,RETURNS(9999)
                      DO 1001 J=1,N
105             1001  PRINT103,(DEL2(J,I),I=1,N)
                      PRINT2016
                2016  FORMAT(//)
                      IF(IVER.EQ.1)STOP
                      IF (IMPRIM.GT.0) PRINT4473,ISP
110                   IF (IMPRIM.GT.0)PRINT510,9
                12    CALL GRAD11,RETURNS(9999)
                      DO 20 I=1,N
                      B(I)=-DEL1(I)
                20    C(I)=B(I)
```

```
      C
      C                                                              +
      C
   40 CALL CHOL(B,DEL2,N)
      IF(IMPRIM.NE.2)GO TO 3596
      DO 3599 I=1,N
      V(I)=0.0
      DO 3598 J=1,N
 3598 V(I)=V(I)+DEL2(I,J)*B(J)
 3599 V(I)=V(I)-C(I)
      PRINT3597,(V(I),I=1,N)
 3597 FORMAT(/1X,'VERIF'/3(5G15.6,/))
 3596 CONTINUE
      C
      C
      C
      SNORM=0.0
      ONORM=0.0
      DO 41 I=1,N
      ONORM=ONORM+C(I)*C(I)
   41 SNORM=SNORM+B(I)*B(I)
      DEL=0.0
      IF(SNORM.EQ.0.0)GO TO 48
      DO 42 I=1,N
      S(I)=B(I)/SQRT(SNORM)
   42 DEL=DEL-S(I)*C(I)
      DELTA=ABS(DEL)/SQRT(ONORM)
      IF(IFIN.NE.0)GO TO 43
      IF(DELTA.GT.TAU1.AND.ONORM.GT.TAU2)GO TO 43
      PRINT105
  105 FORMAT(2X,'OBJECTIVE FUNCTION GRADIENT NO LONGER VARIES')
      GO TO 48
   43 IF(DEL.LT.0.0)GO TO 45
      PRINT113,DEL
  113 FORMAT(2X,'DEL IS POSITIVE, DEL=',G15.5,'******')
      DO 44 I=1,N
   44 S(I)=-S(I)
   45 CONTINUE
      IF(IROPT)6999,6999,7900
 6999 DLAMB=LAMBDA/100.
      CALL POWELL(XLIM,DLAMB,LAMBDA,S,X,N),RETURNS(9999)
      GO TO 7901
 7900 LAMBDA=LAMD
      GO TO 7990
 7999 CONTINUE
      DO 7979 I=1,N
      X(I)=X(I)-DELX(I)
 7979 CONTINUE
      LAMBDA=LAMBDA*.25
      GO TO 7901
 7990 CONTINUE
      DO 7940 I=1,N
      S(I)=B(I)
 7940 CONTINUE
 7901 CONTINUE
      IF(IMPRIM.EQ.2)PRINT800,LAMBDA
  800 FORMAT(4X,'LAMBDA=',G15.5)
```

```
                      DELNOR=0.0
                      DO 46 I=1,N
175                   DELX(I)=LAMBDA*S(I)
                      DELNOR=DELNOR+DELX(I)*DELX(I)
                46    X(I)=X(I)+DELX(I)
                      DELNOR=SQRT(DELNOR)
                      CALL FOBJ(M1,N,X),RETURNS(9999,7999)
180                   IF(M1.LT.M)GO TO 47
                      ICC=ICC+1
                      IF(ICC.LT.20)GO TO 47
                      PRINT108
                108   FORMAT(2X,*THE MINIMIZATION ATTEMPT HAS FAILED*)
                      STOP
185             47    DMM1=M-M1
                      IF(DMM1.LE.0.0)GO TO 7999
                      IF(ABS(DMM1).LT.EPS1.OR.DELNOR.LT.EPS2)GO TO 48
                      IF(IGAIN.EQ.0)GO TO 5330
                      GESP=-0.5*DEL*SQRT(SNORM)*LAMBDA
190                   LAMD=ABS(DMM1/GESP)
                      IF(ABS(GESP).LT.ABS(DMM1))LAMD=LAMD*4.
                      IF(ABS(GESP).GE.ABS(DMM1))LAMD=1.
                      IF(IMPRIM.LT.2)GO TO 5330
                      PRINT5329,DMM1,GESP
195           5329    FORMAT(2X,*M2-M1=*G15.8,*GAIN HOPED FOR=*,G15.8)
              5330    M=M1
                      K=K+1
                      L=L+1
                      IF(NFOBJ.GT.NPMAX)GO TO 999
200                   IF(IMPRIM.LT.2)GO TO 10
                      CALL FEI(K,X,N,M1,NCI,NCE,IF)
                      GO TO 10
                48    K=K+1
                      IF(IMPRIM.GE.1)CALL FEI(K,X,N,M1,NCI,NCE,IF)
205                   IF(INIT.EQ.1)GO TO 504
                      DO 500 I=1,N
                      IF(KX.LT.3.OR.II.EQ.0)GO TO 500
                      XA(I,1)=XA(I,2)
                      XA(I,2)=XA(I,3)
210           500     XA(I,KX)=X(I)
                      IF(KX.LT.3) GO TO 501
                      II=1
                      CAI=1./CA
                5010  CONTINUE
215                   IF(KEX.EQ.0.AND.IF.EQ.0)GO TO 501
                      DO 502 I=1,N
                     X(I)=XA(I,3)+XA(I,1)/CA/CA/CA-XA(I,2)*(CAI*(1.+CAI*(1.+CAI)))
                    1      +XA(I,3)*CAI*(1.+CAI)
                502   CONTINUE
220                   IF(IF.NE.1)GO TO 5020
                      CALL FOBJ(M1,N,X),RETURNS(7963,7963)
                      PRINT5021
                5021  FORMAT(//2X,*ATTEMPT TO IMPROVE RESULT BY EXTRAPOLATION*)
                      CALL FEI(K,X,N,M1,NCI,NCE,IF)
225                   IF=IF+1
                      GO TO 481
                5020  CONTINUE
                      IF(IMPRIM.GE.1)PRINT1652,(X(I),I=1,N)
```

```
                1652  FORMAT(4X,*X AMM *,3G20.12)
230                   IF(IMPRIM.GE.1)PRINT2016
                501   IF(KX.LT.3) KX=KX+1
                504   CONTINUE
                      AI=0.
                      BI=0.
235                   IF(IMET.EQ.0) GO TO 550
                      IF(NCI.EQ.0)GO TO 559
                      DO 551 I=1,NCI
                551   AI=AI-ALOG(G(I,N,X))
                559    IF(NCE.EQ.0)GO TO 558
240                   DO 557I=1,NCE
                557   BI=BI+H(I,N,X)**2
                558   CONTINUE
                      TEST=R*ABS(AI)+BI/R
                      GO TO 552
245             550   CONTINUE
                      IF(NCI.EQ.0) GO TO 560
                      DO 507 I=1,NCI
                      GG=AMIN1(G(I,N,X),0.0)
                507   AI=AI+GG*GG
250             560   CONTINUE
                      IF(NCE.EQ.0)GO TO 569
                      DO 570 I=1,NCE
                      HH=H(I,N,X)
                      AI=AI+HH*HH
255             570   CONTINUE
                569   CONTINUE
                      TEST=ABS(AI/R)
                552   CONTINUE
                      IF(TEST.GE.EPSF)GO TO 5693
260                   IF=1
                      GO TO 480
                5693  R=R/CA
                      ISP=ISP+1
                      IF(IMPRIM.GE.1)PRINT4473,ISP
265             4473  FORMAT(2X,*SUB-PROBLEM NO. *I3)
                      IF(IMPRIM.GE.1)PRINT510,R
                510   FORMAT(6X,*R= *,G15.5)
                      K=0
                      IVEP=0
270                   L=L+1
                      LAMD=1.
                      IF(ISP.GT.1)IGAIN=0
                      IF(ISP.GT.NMAX)GO TO 999
                      GO TO 10
275             480   CONTINUE
                      PRINT2016
                      IF(IMPRIM.EQ.0)CALL FEI(K,X,N,M1,NCI,NCE,IF)
                481   PRINT116,NFOBJ
                116   FORMAT(2X,***OBJECTIVE FUNCTION EVALUATED *,I6,* TIMES*)
280                   IF(KEX.EQ.1.OR.ISP.LT.3)GO TO 7962
                      IF(IF.LT.2)GO TO 5610
                7962  IF(IPROB.GT.1)GO TO 3756
                      STOP
                999   PRINT9753,ISP,NMAX,NFOBJ,NPMAX
285             9753  FORMAT(1X,*ISP=*,I4,3X,*NMAX=*,I4,10X,*NFOBJ=*,I4,3X,*NPMAX=*,I4)
```



```
                      STOP
                7963  PRINT7748
                7748  FORMAT(2X,*EXTRAPOLATION ATTEMPT HAS FAILED*)
                      GO TO 7962
290                   END
```

```
      SUBROUTINE ACTIV(IP)
      COMMON/LOT/ A(10,10),B(10),AA(2),BB(2),W(10,2),Y(10,2)
      COMMON/BAG/ V,T,R,TR,P,RT,NSP,QN(2)
      COMMON/SUMS1/VQ(2,2),G1(15,2),G2(15,15,2)
      DIMENSION DN(10)
      FQ=ALOG(R*T/(P*(V-BB(IP))))
      HQ=ALOG((V+BB(IP))/V)
      D=R*T*TR*BB(IP)
      VC=1./(V-BB(IP))
      VD=1./(V+BB(IP))
      HC=HQ/D
      DPV=-RT*VC**2+AA(IP)*(2*V+BB(IP))*VD**2/(TR*V**2)
      DPV=RT*DPV
      Q1=RT*VC
      Q2=Q1*VC
      Q3=VD/(V*TR)
      DO 55 I=1,NSP
      DN(I)=Q1+B(I)*Q2-Q3*(2*W(I,IP)-AA(IP)*B(I)*VD)
   55 CONTINUE
      DO 20 I=1,NSP
      G1(I,IP)=(FQ+B(I)/(V-BB(IP))+HQ*(-2.*W(I,IP)+AA(IP)*B(I)/BB(I
     +P))-AA(IP)*B(I)/((V+BB(IP))*D)) + ALOG(Y(I,IP)*P)
        CC=1.
      DO 20 J=I,NSP
      Q1=2.*(W(I,IP)*B(J)+W(J,IP)*B(I))
      Q2=AA(IP)*B(I)*B(J)
      G2(I,J,IP)=(1.+(S(I)+B(J))*VC+B(I)*B(J)*VC**2+
     + HC*(-2.*A(I,J)+Q1/BB(IP)-2.*Q2/(BB(IP)**2)) +
     + (-Q1+2.*Q2/BB(IP))*VD/D
     ++ Q2*VD**2/D
     ++(CC-Y(I,IP))/Y(I,IP)+DN(I)*DN(J)/DPV)/QN(IP)
      G2(J,I,IP)=G2(I,J,IP)
      CC=0.
   20 CONTINUE
      RETURN

      END
```

```
      SUBROUTINE CHOL(B,A,N)
      DIMENSION A(25,25),R(25,25),B(25),C(25)
      DMAX=0.0
      DO 2 I=1,N
      DO 2 J=I,N
      IF(ABS(A(I,J)).GT.DMAX)DMAX=ABS(A(I,J))
    2 CONTINUE
      IF(DMAX.EQ.0.0)RETURN
      IF(A(1,1).LE.0.0)GO TO 5
      R(1,1)=SQRT(A(1,1))
    1 CONTINUE
      DO 10 J=2,N
      R(1,J)=0.0
      IF(A(1,J).EQ.0.0)GO TO 10
      R(1,J)=A(1,J)/R(1,1)
   10 CONTINUE
      GO TO 15
    5 R(1,1)=0.0
      DO 6 I=2,N
    6 R(1,1)=R(1,1)+A(1,I)*A(1,I)
      CALL CTION(A(1,1),R(1,1),1,DMAX)
      GO TO 1
   15 DO 30 I=2,N
      MN=I-1
      R(I,I)=0.0
      DO 20 K=1,MN
      IF(R(K,I).EQ.0.0) GO TO 20
      R(I,I)=R(I,I)+R(K,I)*R(K,I)
   20 CONTINUE
      P=A(I,I)-R(I,I)
      IF(P.LE.0.0)GO TO 25
      R(I,I)=SQRT(P)
      GO TO 35
   25 CALL CTION(A(I,I),R(I,I),I,DMAX)
   35 IF(I.EQ.N)GO TO 50
      M=I+1
      DO 30 J=M,N
      R(I,J)=0.0
      DO 40 K=1,MN
      IF(R(K,I).EQ.0.0.OR.R(K,J).EQ.0.0)GO TO 40
      R(I,J)=R(I,J)+R(K,I)*R(K,J)
   40 CONTINUE
   30 R(I,J)=(A(I,J)-R(I,J))/R(I,I)
   50 CONTINUE
      C(1)=B(1)/R(1,1)
      DO 55 I=2,N
      MN=I-1
      P=0.0
      DO 45 K=1,MN
      IF(R(K,I).EQ.0.)GO TO 45
      P=R(K,I)*C(K)+P
   45 CONTINUE
   55 C(I)=(B(I)-P)/R(I,I)
      B(N)=C(N)/R(N,N)
      MN=N-1
      DO 65 I=1,MN
```

SUBROUTINE CHOL

```
      MN=N-I
      MNN=MN+1
      B(MN)=0.0
      DO 75 K=MNN,N
   75 B(MN)=R(MN,K)*B(K)+B(MN)
   65 B(MN)=(C(MN)-B(MN))/R(MN,MN)
      RETURN
      END
```

```
      SUBROUTINE CTION(A,R,I,DMAX)
      COMMON/ECRIT/IMPRIM
      IF (IMPRIM.EQ.2) PRINT100,I
  100 FORMAT(2X,*THE LINE*,I2,* HAS BEEN CORRECTED*)
      DALP=1.1
      DMAXR=SQRT(DMAX)
      IF(ABS(A).GT.R)GO TO 10
      IF(R.EQ.(.0)A=DMAX
      R=ABS(A)+DALP*R
      GO TO 20
   10 A=-A
      R=A-R
   20 R=SQRT(R)
      IF(A.LT.(1.0E-4*DMAXR))R=DMAXR
      RETURN
      END
```

```
      SUBROUTINE DIF1,RETURNS(A1)
      COMMON/DERIV/DEL2(25,25),DEL1(25),X(25),DER(25),N
      DIMENSION A(25)
      DO 10 I=1,N
      A(I)=X(I)
      X(I)=X(I)+DER(I)
      CALL FOBJ(O2,N,X),RETURNS(9999,9999)
      X(I)=A(I)
      X(I)=X(I)-DER(I)
      CALL FOBJ(O1,N,X),RETURNS(9999,9999)
      X(I)=A(I)
   10 DEL1(I)=(O2-O1)/(2.*DER(I))
      RETURN
 9999 RETURN A1
      END
```

```
      SUBROUTINE DIF2,RETURNS(A1)
      COMMON/DERIV/DEL2(25,25),DEL1(25),X(25),DER(25),N
      DIMENSION DELP(25),A(25)
      DO 20 J=1,N
      A(J)=X(J)
      X(J)=X(J)+DER(J)
      CALL GRAD11,RETURNS(9999)
      X(J)=A(J)
      DO 10 I=1,N
   10 DELP(I)=DEL1(I)
      X(J)=X(J)-DER(J)
      CALL GRAD11,RETURNS(9999)
      X(J)=A(J)
      DO 20 I=J,N
   20 DEL2(J,I)=(DELP(I)-DEL1(I))/(2.*DER(J))
      RETURN
 9999 RETURN A1
      END
```

```
      C
      C
            SUBROUTINE ENTREE
            INTEGER EL(10)
            DIMENSION A1(10),B1(10),C1(10),D1(10),DIV(10)
            DIMENSION A(25),B(25),C(25),HREF(25),GREF(25),D(25)
            COMMON/DERIV/DEL2(25,25),DEL1(25),DX(25),DER(25),N
            COMMON/SUMS1/ VQ(2,2),G1(15,2),G2(15,15,2)
            COMMON/SUMG1/COEF(25),Y(25),Z(25),DNOM(25),CM(25,25)
            COMMON/SUMG2/X(25),NSOL
            COMMON/CONT/NCI,NCE,IPROB,IDER
            IF(IPROB.GT.1)GO TO 110
            IPROB=IPROB+1
            NSOL=0
            R=1.9872
            READ(5,*)IFPRNT
            IF (IFPRNT.GT.0) WRITE(6,310)
      310   FORMAT(//* ELEMENT  *,5X,*A*,12X,*B*,12X,*C*,12X,*D*,
           111X,*NUMBER OF ATOMS*/63X,*IN ELEMENT    IN SYSTEM*//)
            DO 5 I=1,NCE
            READ(5,6)EL(I),A1(I),B1(I),C1(I),D1(I),DIV(I),X(I)
            IF (IFPRNT.GT.0) WRITE(6,306)EL(I),A1(I),B1(I),C1(I),
           1D1(I),DIV(I),X(I)
      306   FORMAT(2H  ,A4,3X,4(1X,G12.5),8X,F2.0,3X,G12.5)
      6     FORMAT(A4,6G10.3)
      5     CONTINUE
            READ(5,*)T,PP,REF
      13    FORMAT(3G10.4)
            DEL1(1)=PP
            DEL1(2)=T
            RT=R*T
            ABREF=ABS(REF-T)
            IF(ABREF.LT.10.)GO TO 219
            T2=T*T
            T3=T2*T
            REF2=REF*REF
            REF3=REF2*REF
            DIF1=T-REF
            DIF2=T2-REF2
            DIF3=T3-REF3
            DIF4=(1./T)-(1./REF)
            DIF5=ALOG(T/REF)
            DIF6=(1./T2)-(1./REF2)
            IF (IFPRNT.GT.0) WRITE(6,19)
      19    FORMAT(*1*,/* COMPONENT*,6X,*CPI*,12X,*CPIT*,13X,*CPEL*,12X,
           1*CPELT*,11X,*HTEMP*,12X,*STEMP*//)
      219   CONTINUE
            DO 10 I=1,N
            READ(5,15)DNOM(I),Y(I),Z(I)
      15    FORMAT(A8,2(G10.1))
            IF(Y(I).LT.1..AND.Z(I).LT.1.) NSOL=NSOL+1
            READ(5,*)(CM(I,J),J=1,NCE)
      7     FORMAT(10G10.1)
            READ(5,*)A(I),B(I),C(I),D(I),HREF(I),GREF(I)
      11    FORMAT(6G13.4)
            IF(ABREF.LT.10.) GO TO 217
```

```
      CPI=A(I)*DIF1+(B(I)/2.)*DIF2+(C(I)/3.)*DIF3-D(I)*DIF4
      CPIT=A(I)*DIF5+B(I)*DIF1+(C(I)/2.)*DIF2-(D(I)/2.)*DIF6
   60 CPELT=0.0
      CPEL=0.0
      DO 214 J=1,NCE
      CPEL=CPEL+(CM(I,J)/DIV(J))*(A1(J)*DIF1+(B1(J)/2.)*DIF2+
     1(C1(J)/2.)*DIF3-D1(J)*DIF4)
   65 214  CPELT=CPELT+(CM(I,J)/DIV(J))*(A1(J)*DIF5+B1(J)*DIF1+(C1(J)/2.)*
     1DIF2-(D1(J)/2.)*DIF6)
      SREF=(HREF(I)-GREF(I))/REF
      HTEMP=HREF(I)+CPI-CPEL
      STEMP=SREF+CPIT-CPELT
   70 COEF(I)=(HTEMP-T*STEMP)/RT
      ABCO=ABS(CCEF(I))
      IF(ABCO.LE.1.E-05)COEF(I)=0.0
      IF (IFPRNT.GT.0) WRITE(6,17)DNOM(I),CPI,CPIT,CPEL,CPELT,
     1HTEMP,STEMP
   75 17   FORMAT(≠ ≠,1X,A8,6(1X,G15.8))
      GO TO 10
      217  CCEF(I)=GREF(I)/RT
      10   CONTINUE
      IF (IFPRNT.GT.0) WRITE(6,9)
   80 9    FORMAT(≠0≠,/≠ COMPONENT≠,5X,≠A≠,12X,≠B≠,12X,≠C≠,12X,≠D≠,11X,
     1≠HREF≠,10X,≠GREF≠,11X,≠U/RT≠//)
      DO 18 K=1,N
      IF (IFPRNT.GT.0) WRITE(6,12)DNOM(K),A(K),B(K),C(K),D(K),
     1HREF(K),GREF(K),COEF(K)
   85 12   FORMAT(≠ ≠,A8,4(1X,G12.5),2(1X,G13.6),1X,G14.7,1X,F6.4)
      18   CONTINUE
      IF (IFPRNT.GT.0) WRITE(6,20)T,PP,REF
      20   FORMAT(///≠ TEMP.= ≠,F6.1,≠ KELVIN≠/≠ PRESSURE= ≠,F6.1,
     1≠ ATM.≠/≠ REF. TEMP.= ≠,F6.1,≠ KELVIN≠/)
   90 IF (IFPRNT.GT.0) WRITE(6,51) (EL(J),J=1,NCE)
      51   FORMAT(≠0≠/≠ COMPONENT   Y      Z≠,4X,≠NUMBER OF ATOMS FOR EACH ≠,
     1≠ELEMENT ≠/21X,10A4/)
      DO 16 I=1,N
      IF (IFPRNT.GT.0) WRITE(6,52)DNOM(I),Y(I),Z(I),(CM(I,J)
   95 1,J=1,NCE)
      52   FORMAT(≠ ≠,A8,1X,12(1X,F4.1))
      16   CONTINUE
      IF (IFPRNT.GT.0) WRITE(6,50)
      50   FORMAT(/////)
  100 RETURN
      110  TOTGAZ=0.
      TOTSYS=0.
      DO 111 I=1,N
      TOTSYS=TOTSYS+DX(I)
  105 111  TOTGAZ=TOTGAZ+Y(I)*DX(I)
      WRITE(6,112)TOTSYS,TOTGAZ
      112  FORMAT(//////≠ NO. OF MOLES IN CHEMICAL SYSTEM =≠,G12.5/
     1≠ NO. OF MOLES IN GAS PHASE= ≠,G12.5/)
      WRITE(6,113)
  110 113  FORMAT(///12X,≠ MOLAR PERCENTAGES≠,25X,≠ NO. MOLES≠/15X,
     1≠SYSTEM       GASEOUS        CARBON≠)
      PERCAR=0.
      DO 115 I=1,N
      IF(X(1).LE.0.) GO TO 116
```

```
      PERCAR=DX(I)*100.*CM(I,1)/X(1)
  116 PERGAZ=DX(I)*Y(I)*100./TOTGAZ
      PERSYS=DX(I)*100./TOTSYS
      WRITE(6,114)CNOM(I),PERSYS,PERGAZ,PERCAR,DX(I)
  114 FORMAT(' ',A8,4(3X,G12.5))
  115 CONTINUE
      WRITE(6,120)
  120 FORMAT(//////)
      CALL PCENT
      NP=(N-NSOL)/2
      PRINT 400,((VO(I,J),I=1,2),J=1,2)
  400 FORMAT(2X,'VOL GAS =',G14.6,'RK VG =',G14.6,'VOL LIQ =',
     *G14.6,'RK VL =',G14.6//)
      PRINT 710
      PRINT 720,(G1(I,1),I=1,NP)
      PRINT 730
      PRINT 720,(G1(I,2),I=1,NP)
  710 FORMAT(2X,'GAS PHASE POTENTIALS'/)
  730 FORMAT(2X,'LIQUID PHASE POTENTIALS'/)
  720 FORMAT(2X,8G14.7//)
      PRINT 740
      CALL PRMT(G2,15,NP,1)
      PRINT 750
      CALL PRMT(G2,15,NP,2)
  740 FORMAT(2X,'D2G/DN2 FOR GAS PHASE '/)
  750 FORMAT(2X,'G2G/DN2 FOR LIQUID PHASE '/)
      STOP 999
      END
```

```
      C
      C                                                                 -
      C
            SUBROUTINE FEI(K,X,N,M1,NCI,NCE,IF)
            REAL M1
            DIMENSION X(N),VH(50),VG(50)
            IF (IF.LE.0)PRINT109,K
            PRINT110,(X(I),I=1,N)
            PRINT133,M1
            VM1F=F(N,X)
            PRINT3100,VM1F
      3100  FORMAT(2X,*VALUE FOR F =,G14.7)
      133   FORMAT(2X,*M=*,G14.7)
            IF(NCE.EQ.0)GO TO 7800
            DO 7801 I=1,NCE
      7801  VH(I)=H(I,N,X)
            PRINT7803
            PRINT7802,(VH(I),I=1,NCE)
      7802  FORMAT(1X,4(G15.5,2X))
      7803  FORMAT(2X,*VALUE FOR THE EQUALITY CONSTRAINTS *)
      7800  CONTINUE
            IF(NCI.EQ.0)GO TO 7804
            DO 7805 I=1,NCI
      7805  VG(I)=G(I,N,X)
            PRINT7806
      7806  FORMAT(2X,*VALUE FOR THE INEQUALITY CONSTRAINTS *)
            PRINT7802,(VG(I),I=1,NCI)
      7804  CONTINUE
      109   FORMAT(5X,*ITERATION NUMBER*,I3)
      110   FORMAT(1X,*X(I)=*/5(5(G14.7)/))
            PRINT1
      1     FORMAT(/)
            RETURN
            END


      1
              FUNCTION F(NQ,PX)

            COMMON/SUMG1/COEF(25),Y(25),Z(25),ONOM(25),CM(25,25)
            DIMENSION PX(25)
      5     COMMON/SUMG2/X(25),NSOL
            COMMON/DERIV/ DEL2(25,25),DEL(25),DX(25),DER(25),N
            COMMON/SUMS1/ VQ(2,2),G1(15,2),G2(15,15,2)
            F=0.0
            NP=(N-NSOL)/2
     10     NP1=NP+1
            CALL POINT
            DO 30 MM=1,N
            II=MM
            IP=1
     15     IF(MM.LT.NP1) GO TO 25
            II=MM-NP
            IP=2
     25     F=F+(COEF(MM)+G1(II,IP))*DX(MM)
     30     CONTINUE
     20     RETURN
            END
```

```
      C
      C
      SUBROUTINE FOBJ(FOB,N,X),RETURNS(A1,A2)
      COMMON/CONT/NCI,NCE,IPROB,IDER
      COMMON/FOACT/NFOBJ
      COMMON/ACC/R,ITIT
      COMMON/CHCIX/IMET,IPOS
      DIMENSION X(25)
      IF(IMET.EQ.1)GO TO 100
      FOB=F(N,X)
      IF(NCI.EQ.0) GO TO 12
      DO 10 I=1,NCI
      GG=G(I,N,X)
   10 FOB=FOB+AMIN1(0.,GG)*AMIN1(0.,GG)/R
   12 CONTINUE
      IF(NCE.EQ.0) GO TO 13
      DO 11 I=1,NCE
   11 FOB=FOB+H(I,N,X)*H(I,N,X)/R
   13 NFOBJ=NFOBJ+1
      RETURN
  100 CONTINUE
      IF(INIT.EQ.0) GO TO 1
      AI=0.0
      FOB=0.0
      IF(IPOS.EQ.0) GO TO 4000
      DO 2002 I=1,N
      GN=X(I)
      IF(GN.GT.0.) GO TO 2003
      AI=-GN+AI
      FOB=AI
      GO TO 2002
 2003 FOB=-R*ALOG(GN)+FOB
 2002 CONTINUE
 4000 CONTINUE
      IF(NCI.EQ.0)GO TO 4
      DO 2 I=1,NCI
      GG=G(I,N,X)
      IF(GG.GT.0.) GO TO 3
      IF (GG.EQ.0.) GG=-1.E-20
      AI=-GG+AI
      FOB=AI
      GO TO 2
    3 FOB=-R*ALOG(GG)+FOB
    2 CONTINUE
      IF(ABS(FOB).GT.1.E+50) FOB=1.E+50
      IF(AI.EQ.0.) GO TO 4
      RETURN
    4 PRINT6
    6 FORMAT(/* THE NEW STARTING POINT IS*/* X(I)=1,N *)
      PRINT5,(X(I),I=1,N)
    5 FORMAT(5(2X,5G15.5/))
      INIT=0
      RETURN A1
    1 CONTINUE
      FOB=0.
```

```
      SUBROUTINE FOBJ
                  IF(IPCS.EQ.0) GO TO 3000
                  DO 3015 I=1,N
   60             GN=X(I)
                  IF(GN.LT.1.E-50) RETURN A2
            3015  FOB=FOB-R*ALOG(GN)
            3000  CONTINUE
                  FOB=FOB+F(N,X)
   65             IF(NCI.EQ.0)GO TO 101
                  DO 15 I=1,NCI
                  GG=G(I,N,X)
                  IF(GG.LE.1.E-50) RETURN A2
      15          FOB=FOB-ALOG(GG)*R
   70       101   CONTINUE
                  IF(NCE.EQ.0)GO TO 102
                  DO 16 I=1,NCE
      16          FOB=FOB+H(I,N,X)*H(I,N,X)/R
      102         CONTINUE
   75             IF(ABS(FOB).GT.1.E+50) FOB=1.E+50
                  NFOBJ=NFOBJ+1
                  RETURN
                  END
```

```
      SUBROUTINE FPO(FOP,S,X,DL,N),RETURNS(A1,A2)
      DIMENSION A(25),X(25),S(25)
      DO 10 I=1,N
10    A(I)=X(I)+DL*S(I)
      CALL FOBJ(FOP,N,A),RETURNS(9999,1111)
      FOP=-FOP
      RETURN
9999  CONTINUE
      DO 20 I=1,N
20    X(I)=A(I)
      RETURN A1
1111  RETURN A2
      END

        FUNCTION G(I,N,DX)
      DIMENSION CX(25)
      DIMENSION U(25)
      G=0.
      DO 1 K=1,N
      U(K)=0.
      IF(K.EQ.I) U(K)=1.
1     G=G+DX(K)*U(K)
      RETURN
      END

      SUBROUTINE GRAD1(IN),RETURNS(A1)
      COMMON/SUMG1/COEF(25),Y(25),Z(25),DMON(25),CM(25,25)
      COMMON/DERIV/DEL2(25,25),DEL(25),DX(25),DER(25),N
      COMMON/SUMG2/X(25),NSOL
      COMMON/SUMS1/ V0(2,2),G1(15,2),G2(15,15,2)
      IF(IN.GT.1)GO TO 3
      CALL PCINT
      NP=(N-NSOL)/2
      DO 15 I=1,N
      IF(I.GT.NP) GO TO 16
      DEL(I)=G1(I,1)+COEF(I)
      GO TO 15
   16  II=I-NP
15    DEL(I)=G1(II,2)+COEF(I)
   15  CONTINUE
      RETURN
3     CONTINUE
      DO 22 MM=1,N
22    DEL(MM)=CM(MM,IN-1)
      RETURN
9999  RETURN A1
      END
```

```
      1
                      SUBROUTINE GRAD11,RETURNS(A1)
                      COMMON/DERIV/DEL2(25,25),DEL1(25),X(25),DER(25),N
                      COMMON/CONT/NCI,NCE,IPROB,IDER
      5               COMMON/ACC/R,INIT
                      COMMON/CHOIX/IMET,IPOS
                      DIMENSION AU(25)
                      IF(INIT.EQ.1.OR.IDER.GT.1) GO TO 99
                98    NCIP1=NCI+1
     10               NCIP2=NCI+2
                      NCEP=NCE+NCI+1
                      CALL GRAD1(1),RETURNS(9999)
                      DO 1 I=1,N
                1     AU(I)=DEL1(I)
     15               IF(NCI.EQ.0) GO TO 10
                      DO 2 K=2,NCIP1
                      CALL GRAD1(K),RETURNS(9999)
                      KK=K-1
                      IF(IMET.EQ.1)GO TO 30
     20               GG=AMIN1(0.,G(KK,N,X))
                      IF(GG.EQ.0.0)GO TO 2
                      DO 3 I=1,N
                3     AU(I)=AU(I)+2.*GG*DEL1(I)/R
                      GO TO 2
     25         30    DO 31 I=1,N
                31    AU(I)=AU(I)-DEL1(I)*R/G(KK,N,X)
                2     CONTINUE
                10    CONTINUE
                      IF(NCE.EQ.0)GO TO 20
     30               DO 4 K=NCIP2,NCEP
                      KK=K-NCIP1
                      CALL GRAD1(K),RETURNS(9999)
                      DO 5 I=1,N
                5     AU(I)=AU(I)+2.*H(KK,N,X)*DEL1(I)/R
     35         4     CONTINUE
                20    CONTINUE
                      IF(IPOS.EQ.0) GO TO 42
                      IF(IMET.EQ.0) GO TO 41
                      DO  40 I=1,N
     40   *    40    AU(I)=AU(I)-R/(X(I)-1.E-20)
NOTE        CONSTANT TERM OF ZERO -- IGNORED
                      GO TO 42
                41    CONTINUE
                      DO 50 I=1,N
     45               GN=AMIN1(0.,X(I))
                50    AU(I)=AU(I)+2./R*GN
                42    CONTINUE
                      DO 21 I=1,N
                      DEL1(I)=AU(I)
                21    CONTINUE
     50               RETURN
                99    CALL DIF1,RETURNS(9999)
                      RETURN
                9999  RETURN A1
                      END
```

```
      1
                SUBROUTINE GRAD2(IN),RETURNS(A1)
                COMMON/SUMG1/COEF(25),Y(25),Z(25),DNOM(25),GM(25,25)
                COMMON/DERIV/DA(25,25),DEL(25),DX(25),DER(25),N
      5         COMMON/SUMG2/ X(25),NSOL
                COMMON/SUMS1/ VQ(2,2),G1(15,2),G2(15,15,2)
                IF(IN.GT.1)GO TO 5
                CALL POINT
                NP=(N-NSOL)/2
     10         DO 25 I=1,N
                II=I
                IF(I.GT.NP) II=I-NP
                 DO 25 J=I,N
                  JJ=J
     15           IF(J.GT.NP) JJ=J-NP
                  IF(JJ.NE.J) GO TO 30
                   DA(I,J)=G2(II,JJ,1)
                GO TO 25
           30    IF(II.NE.I) GO TO 31
     20           DA(I,J)=0.
                   GO TO 25
            31     DA(I,J)=G2(II,JJ,2)
            25     CONTINUE
                RETURN
     25       5    CONTINUE
                  DO 40 I=1,N
                  DO 40 J=I,N
                40  DA(I,J)=0.
                  RETURN
     30         9999 RETURN A1
                  END
```

```
      1
                        SUBROUTINE GRAD22,RETURNS(A1)
                        COMMON/DERIV/DEL2(25,25),DEL1(25),X(25),DER(25),N
                        COMMON/CONT/NCI,NCE,IPOS,IDER
      5                 COMMON/ACC/R,INIT
                        COMMON/CHOIX/IMET,IPOS
                        DIMENSION AU(25,25)
                        IF(INIT.EQ.1.OR.IDER.GT.0) GO TO 99
                  98    NCIP1=NCI+1
     10                 NCIP2=NCI+2
                        NCEP=NCI+NCE+1
                        CALL GRAD2(1),RETURNS(9999)
                        DO 1 I=1,N
                        DO 1 J=I,N
     15           1     AU(I,J)=DEL2(I,J)
                        IF(NCI.EQ.0) GO TO 10
                        DO 2 K=2,NCIP1
                        CALL GRAD1(K),RETURNS(9999)
                        CALL GRAD2(K),RETURNS(9999)
     20                 KK=K-1
                        IF(IMET.EQ.1)GO TO 30
                        GG=AMIN1(0.,G(KK,N,X))
                        IF(GG.EQ.0.0)GO TO 2
                        DO 3 I=1,N
     25                 DO 3 J=I,N
                  3     AU(I,J)=AU(I,J)+2.*(DEL1(I)*DEL1(J)+DEL2(I,J)*GG)/R
                        GO TO 2
                  30    DO 32 I=1,N
                        DO 32 J=I,N
     30                 GG=G(KK,N,X)
                  32    AU(I,J)=AU(I,J)-R*(GG*DEL2(I,J)-DEL1(I)*DEL1(J))/GG/GG
                  2     CONTINUE
                  10    CONTINUE
                        IF(NCE.EQ.0) GO TO 20
     35                 DO 4 K=NCIP2,NCEP
                        KK=K-NCIP1
                        CALL GRAD1(K),RETURNS(9999)
                        CALL GRAD2(K),RETURNS(9999)
                        DO 5 I=1,N
     40                 DO 5 J=I,N
                  5     AU(I,J)=AU(I,J)+2.*(DEL1(I)*DEL1(J)+DEL2(I,J)+H(KK,N,X))/R
                  4     CONTINUE
                  20    CONTINUE
                        IF(IPOS.EQ.0) GO TO 42
     45                 IF(IMET.EQ.0) GO TO 41
                        DO 40 I=1,N
                  40    AU(I,I)=AU(I,I)+R/(X(I)-0.E-20)/(X(I)-0.E-20)
NOTE     *              CONSTANT TERM OF ZERO -- IGNORED
NOTE     *              CONSTANT TERM OF ZERO -- IGNORED
                        GO TO 42
                  41    DO 50 I=1,N
     50           50    AU(I,I)=AU(I,I)+2.*GG/X(I)/R
                  42    CONTINUE
                        DO 21 I=1,N
                        DO 21 J=I,N
                  21    DEL2(I,J)=AU(I,J)
     55                 RETURN
```

```
      SUBROUTINE GRAD22

                  99    CALL DIF2,RETURNS(9999)
                        RETURN
                  9999  RETURN A1
                        END
```

```
      FUNCTION H(IN,N,DX)
      COMMON/SUMG1/COEF(25),Y(25),Z(25),DNCM(25),CM(25,25)
      COMMON/SUMG2/X(25),NSOL
      DIMENSION DX(25)
      H=0.
      DO 14 MM=1,N
   14 H=H+CM(MM,IN)*DX(MM)
      H=H+X(IN)
      RETURN
      END
```

```
      SUBROUTINE MODEL
      DIMENSION C(4),Z(3),GG(10)
      COMMON/LCT/ A(10,10),B(10),AA(2),BB(2),W(10,2),Y(10,2)
      COMMON/BAG/ J,T,R,TR,P,RT,NSP,GG(2)
      COMMON/SUMS2/ XX(25),NSOL
      COMMON/SUMS1/ VG(2,2),G1(15,2),G2(15,15,2)
      COMMON/DERIV/ DA(25,25),DEL(25),DX(25),DER(25),NTOT
      COMPLEX Z
      NSP=(NTOT-NSOL)/2
      NDEG=3
      R=1.98719
      P=DEL(1)
      T=DEL(2)
      DO 348 I=1,NSP
      READ *,A(I,I),B(I)
  348 CONTINUE
      DO 446 I=1,15
      DO 446 J=1,15
      G1(I,1)=G1(I,2)=0.
      G2(I,J,1)=G2(I,J,2)=0.
  446 CONTINUE
      DO 12 I=1,NSP
      DO 12 J=I,NSP
      IF(I.EQ.J) GO TO 12
      A(I,J)=SQRT(A(I,I)*A(J,J))
      A(J,I)=A(I,J)
   12 CONTINUE
      RT=R*T
      TR=SQRT(T)
      RETURN
      ENTRY POINT
      GG(2)=0.
      GG(1)=0.
      DO 40 I=1,NSP
      I7=7+NSP
      Y(I,1)=DX(I)
      Y(I,2)=DX(I7)
      GG(1)=GG(1)+DX(I)
      GG(2)=GG(2)+DX(I7)
   40 CONTINUE
      DO 45 I=1,NSP
      Y(I,1)=Y(I,1)/GG(1)
      Y(I,2)=Y(I,2)/GG(2)
   45 CONTINUE
      DO 100 IP=1,2
      AA(IP)=0.
      BB(IP)=0.
      DO 25 I=1,NSP
      W(I,IP)=0.
      BB(IP)=BB(IP)+Y(I,IP)*B(I)
      DO 25 J=1,NSP
      W(I,IP)=W(I,IP)+Y(J,IP)*A(J,I)
      AA(IP)=AA(IP)+Y(I,IP)*A(I,J)*Y(J,IP)
   25 CONTINUE
      C(1)=P*TR
      C(2)=-R*T*TR
      C(3)=-(P*TR*BB(IP)**2+R*T*TR*BB(IP)-AA(IP))
```

SUBROUTINE MODEL

```
      C(4)=-AA(IP)*BB(IP)
      CALL ZPOLR(C,NDEG,Z,IR)
      V=Z(1)
      IF(IP.EQ.2) V=Z(3)
      VG(IP,1)=V
      VG(IP,2)=V-BB(IP)
      IF(V.LT.BB(IP)) GO TO 845
      CALL ACTIV(IP)
      GO TO 100
  845 CALL PHASE(IP)
  100 CONTINUE
      DG=0.
      END
```

```
      SUBROUTINE PHASE(IP)
      COMMON/SUMS1/ VQ(2,2),G1(15,2),G2(15,15,2)
      DO 150 I=1,15
      G1(I,IP)=ABS(G1(I,IP))
      DO 150 J=1,15
      G2(I,J,IP)=ABS(G2(I,J,IP))
  150 CONTINUE
      RETURN
      END
```

beam

```
      SUBROUTINE POWELL(XLIM,DELX,X1,S,X,N),RETURNS(A1)
      DIMENSION ZZ(3),WW(3),YF(3),X(25),S(25)
      DELX1=DELX
 1945 CALL FPO(Y1,S,X,X1,N),RETURNS(9999,220)
      DELX1=DELX
      X2=X1+DELX
      II=1
    8 CALL FPO(Y2,S,X,X2,N),RETURNS(9999,220)
    9 IF(Y2-Y1)10,12,12
   10 IF(II-1)14,14,16
   14 II=II+1
      DELX=-DELX
      X2=X1+DELX
      GO TO 8
   16 GO TO 80
   12 CONTINUE
      X3=X2+DELX
      GO TO 13
   17 X3=X4
      Y3=Y4
      GO TO 133
   13 CALL FPO(Y3,S,X,X3,N),RETURNS(9999,220)
  133 DELX=2.*DELX
  223 X4=X3+DELX
      CALL FPO(Y4,S,X,X4,N),RETURNS(9999,221)
      GO TO 222
  221 DELX=DELX*0.75
      GO TO 223
  222 IF(Y4-Y3)90,220,17
   80 ZZ(1)=X1
      ZZ(2)=X1+DELX/2.
      ZZ(3)=X2
      GO TO 99
   90 ZZ(1)=X3
      ZZ(2)=X3+DELX/2.
      ZZ(3)=X4
      GO TO 99
  220 DELX=DELX1/10.
      X1=X1/10.
      GO TO 1945
   99 DO 97 I=1,3
      CALL FPO(YF(I),S,X,ZZ(I),N),RETURNS(9999,220)
   97 CONTINUE
   98 A=ZZ(2)-ZZ(3)
      B=ZZ(3)-ZZ(1)
      C=ZZ(1)-ZZ(2)
      D=ZZ(2)+ZZ(2)-ZZ(3)*ZZ(3)
      E=ZZ(3)*ZZ(3)-ZZ(1)*ZZ(1)
      F=ZZ(1)*ZZ(1)-ZZ(2)*ZZ(2)
      ZZT=.5*(D*YF(1)+E*YF(2)+F*YF(3))
      ZZB=A*YF(1)+B*YF(2)+C*YF(3)
      ZZM=ZZT/ZZB
      CALL FPO(YFM,S,X,ZZM,N),RETURNS(9999,220)
      IF(ABS(YFM-YF(1))/ABS(YF(1)).GT.100.)GO TO 1947
      DO 100 J=1,3
      WW(J)=ABS(ZZ(J)-ZZM)/1.
```

```
NOTE      *          DIVIDE BY 1 -- IGNORED
                     IF(WW(J)-XLIM) 105,105,106
                105  XMAX=ZZ(J)
      60             GO TO 200
                106  CONTINUE
                100  CONTINUE
                     IF(YF(2)-YF(1))110,111,111
                111  IF(YF(3)-YF(1))110,113,113
      65        110  IF(YF(3)-YF(2))115,114,114
                113  JK=1
                     GO TO 117
                114  JK=2
                     GO TO 117
      70        115  JK=3
                117  ZZ(JK)=ZZM
                     YF(JK)=YFM
                     GO TO 98
                200  X1=XMAX
      75             CALL FPO(Y1,S,X,X1,N),RETURNS(9999,220)
                     RETURN
                1947 YMAXI=AMAX1(YF(1),YF(2),YF(3))
                     DO 1948 I=1,3
                     IF(YF(I).EQ.YMAXI)GO TO 1949
      80        1948 CONTINUE
                1949 X1=ZZ(I)
                     DELX=DELX1
                     GO TO 1945
                9999 RETURN A1
      85             END
```

```
      SUBROUTINE PRMT (A,M,NC,NS)
      DIMENSION A(M,M,2)
C
C     PRMT SIMPLY PRINTS ONE SHEET OF A TENSOR
C
      L=(NC-1)/10+1
      JH=0
      DO 1 I1=1,L
      JL=JH+1
      JH=JL+9
      IF (I1.EQ.L) JH=NC
      PRINT 2, (J,J=JL,JH)
      DO 1 I=1,NC
    1 PRINT 3, I,(A(I,J,NS),J=JL,JH)
      RETURN
    2 FORMAT (1H )2X10I12)
    3 FORMAT (5XI2,10(2XF10.6))
      END
```

PROGRAMME PARAMETERS

N= 21 NCI= 0 NCE= 3
IMET= 1 IPOS= 1 LECT= 1 IMPRIM= 1 IDER= 0
IROPT= 1 IGAIN= 1 K1= 1 IVER= 0 KEX= 0 IPROB= 1
R= 1.00 CA= 4.00 NMAX= 20 NPMAX=3000
IFIN= 1
TAU1= .1000000E-04 TAU2= .1000000E-04
EPS1= .1000000E-05 EPS2= .1000000E-09
EPSF= .1000000E-04
DIVE= .1000000E-05 XLIM= .1000000E-05

INITIAL ESTIMATES FROM 1 TO N

1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
1.0000	1.0000	9.0000					

ELEMENT	A	B	C	D	NUMBER OF ATOMS IN ELEMENT	IN SYSTEM
C	4.0300	.11400E-07	0.	-.20400E+06	1.	15.940
H	6.5200	.78000E-03	0.	12000.	2.	20.960
O	7.1600	.10000E-02	0.	-45000.	2.	14.770

COMPONENT	CPI	CPIT	CPEL	CPELT	HTEMP	STEMP
H2(G)	3083.7895	6.3282113	3083.7895	6.3282113	0.	0.
CO(G)	3202.8964	6.5536580	3290.[illegible]	6.5671240	-26503.123	21.314649
CO2(G)	4630.1019	9.3057274	4946.4673	9.9632277	-64367.365	-.83055518
CH4(G)	5089.5130	11.260032	7601.2537	15.652443	-20600.641	-25.084651
H2O(G)	3766.8434	7.6763703	4746.2359	9.7091150	-58769.392	-12.641699
C10H8O2G	27921.588	55.710503	31983.797	64.135256	-53762.209	-95.122078
C14H10O3	35767.074	71.738721	43258.331	86.668652	-82461.256	-130.32518
C6H6O G	46242.217	90.648436	20779.262	41.601860	2502.9547	-1.6338833
C6H12C G	26691.500	54.346731	29966.631	60.586494	-73669.131	-147.88634
C7H6O2 G	18495.731	38.289492	23939.283	48.138984	-74953.553	-74.060585
H2(L)	3083.7895	6.3282113	3083.7895	6.3282113	0.	0.
CO(L)	3202.8964	6.5536580	3290.[illegible]	6.5671240	-26503.123	21.314649
CO2(L)	4630.1019	9.3057274	4946.4673	9.9632277	-94367.365	-.83055518
CH4(L)	5089.5130	11.260032	7601.2537	15.652443	-20600.641	-25.084651
H2O(L)	3766.8434	7.6763703	4746.2359	9.7091150	-59769.392	-12.641699
C10H8O2L	27921.588	55.710503	31983.797	64.135256	-53762.209	-95.122078
C14H10O3	35767.074	71.738721	43258.331	86.668652	-82461.256	-130.32518
C6H6O L	46242.217	90.648436	20779.262	41.601860	2502.9547	-1.6338833
C6H12OL	26691.500	54.346731	29966.631	60.586494	-73669.131	-147.88634
C7H6O2L	18495.731	38.289492	23939.283	48.138984	-74953.553	-74.060585
C(S)	1633.5746	3.2160204	1633.5746	3.2160204	0.	0.

COMPONENT	A	B	C	D	HREF	GREF	U/RT
H2(G)	6.5220	.78000[illegible]E-03	0.	-12000.	0.	0.	0.
CO(G)	6.7600	.98000[illegible]E-03	0.	-11000.	-26416.0	-32781.0	-20.
CO2(G)	10.570	.21000[illegible]E-02	0.	-.26660E+06	-94051.0	-94000.0	-63.74833
CH4(L)	3.3416	.16044[illegible]E-01	-.43000E-05	0.	-17889.0	-12140.0	-63.75448
H2O(L)	7.2600	.22300[illegible]E-02	-.28300E-06	0.	-57798.0	-54635.0	-1.385896
C10H8O2L	26.900	.84000[illegible]E-01	-.25900E-04	0.	-49700.0	-23850.0	-33.60326
C14H10O3	38.710	.10700	-.46560E-04	0.	-74970.0	-40550.0	11.30960
C6H6O L	30.480	.14290	0.	0.	-23030.0	-7869.09	9.506364
C6H12OL	26.524	.11900	-.97600E-04	0.	-70400.0	-28180.0	2.524283
C7H6O2L	21.258	.95600E-01	-.10120E-03	0.	-69360.0	-50296.0	-24.32239
C(S)	4.0300	.11400E-02	0.	-.20400E+06	0.	0.	-13.78169

TEMP.= 740.0 KELVIN.
PRESSURE= 250.0 ATM.
REF. TEMP.= 298.2 KELVIN

```
COMPONENT  Y     Z     NUMBER OF ATOMS FOR EACH ELEMENT
                                  C     H     O
 H2(G)       1.0   0.0   0.0   0.0   2.0   0.0
 CO(G)       1.0   0.0   0.0   1.0   0.0   1.0
 CO2(G)      1.0   0.0   0.0   1.0   0.0   2.0
 CH4(G)      1.0   0.0   0.0   1.0   4.0   0.0
 H2O(G)      1.0   0.0   0.0   0.0   2.0   1.0
C10H8O2G     1.0   0.0   0.0  10.0   8.0   2.0
C14H10O3     1.0   0.0   0.0  14.0  10.0   3.0
C6H6O  G     1.0   0.0   0.0   6.0   6.0   1.0
C6H12O G     1.0   0.0   0.0   6.0  12.0   6.0
C7H6O2 G     1.0   0.0   0.0   7.0   6.0   2.0
 H2(L)       0.0   1.0   0.0   0.0   0.0   0.0
 CO(L)       0.0   1.0   0.0   0.0   0.0   0.0
 CO2(L)      0.0   1.0   0.0   0.0   0.0   0.0
 CH4(L)      0.0   1.0   0.0   0.0   0.0   0.0
 H2O(L)      0.0   1.0   0.0   0.0   0.0   0.0
C10H8O2L     0.0   1.0   0.0  10.0   8.0   2.0
C14H10O3     0.0   1.0   0.0  14.0  10.0   3.0
C6H6O  L     0.0   1.0   0.0   6.0   6.0   1.0
 C6H12OL     0.0   1.0   0.0   6.0  12.0   6.0
 C7H6O2L     0.0   1.0   0.0   7.0   6.0   2.0
 C(S)        0.0   0.0   1.0   0.0   0.0   0.0


 SUB-PROBLEM NO.    1
    P=        1.0000

THE NEW STARTING POINT IS
X(I)=1,N
      1.0000          1.0000          1.0000          1.0000          1.0000
      1.0000          1.0000          1.0000          1.0000          1.0000
      1.0000          1.0000          1.0000          1.0000          1.0000
      1.0000          1.0000          1.0000          1.0000          1.0000
      6.3160
    ITERATION NUMBER 25
X(I)=
 .4769495        .3796977        16.40613        .7179112        7.550793
 .1413328E-01    .1008829E-01    .3286046E-01    .1851729E-01    .2283867E-01
 .6061232E-01    .6752963E-01    .1268565        .7751935E-01    .1604969
 .8682604E-02    .6730853E-02    .1922096E-01    .1274855E-01    .1387736E-01
 3.141032
M= -848.5704
VALUE FOR F  -848.4538
VALUE FOR THE EQUALITY CONSTRAINTS
 .15918338          .18674321E-01     14.667452


 SUB-PROBLEM NO.    2
    P=        .2500
    ITERATION NUMBER  8
X(I)=
 .2462635        .1381166        5.133041        1.011262        7.905664
 .3886210E-02    .2746574E-02    .9025357E-02    .5316509E-02    .6167841E-02
 .2439862E-01    .1685114E-01    .2622536E-01    .2257446E-01    .4318923E-01



 .2354361E-02    .1765023E-02    .4985503E-02    .3450942E-02    .3656333E-02
 6.275463
M= -463.1040
VALUE FOR F  -535.9062
VALUE FOR THE EQUALITY CONSTRAINTS
 .33669622E-02    -.42896463E-01     3.7067226
```

```
 SUB-PROBLEM NO.   3
    P=          .6250CE-01
    ITERATION NUMBER  5
X(I)=
 .1486608        .5255557E-01  3.838678       1.163109       7.923793
 .1005374E-02    .7048469E-03  .2422997E-02   .1466268E-02   .1616561E-02
 .5223342E-02    .4193373E-02  .6449101E-02   .5676338E-03   .1021698E-02
 .5944309E-03    .4446015E-03  .1237349E-02   .8782993E-03   .9220658E-03
 11.78379
 M= -436.7241
 VALUE FOR F   -456.3747
 VALUE FOR THE EQUALITY CONSTRAINTS
  .18111668E-03   -.13971634E-01     .92948828

 SUB-PROBLEM NO.   4
    P=          .1662SE-01
    ITERATION NUMBER  5
X(I)=
 .1155502        .2709790E-01  3.526027       1.216911       7.911865
 .2578112E-03    .1754439E-03  .6424534E-03   .3650246E-03   .4201767E-03
 .1564348E-02    .1046888E-02  .1646647E-02   .1454746E-02   .2769865E-02
 .1489080E-03    .1113556E-03  .3103515E-03   .2206947E-03   .2310080E-03
 11.14461
 M= -431.1067
 VALUE FOR F   -436.3615
 VALUE FOR THE EQUALITY CONSTRAINTS
  .1095112E-04   -.37063662E-02     .23256917

 SUB-PROBLEM NO.   5
    P=          .38063E-02
    ITERATION NUMBER  4
X(I)=
 .1553806        .1855230E-01  3.449084       1.230438       7.906521
 .5609129E-04    .4662169E-04  .1702356E-03   .9443869E-04   .1090946E-03
 .3916726E-03    .2616265E-03  .4206810E-03   .3722102E-03   .6933923E-03
 .3724556E-04    .2765184E-04  .7765216E-04   .5521373E-04   .5778366E-04
 11.23628
 M= -428.2497
 VALUE FOR F   -431.3462
 VALUE FOR THE EQUALITY CONSTRAINTS
  .6790656AE-06   -.94018225E-03     .58154757E-01

 SUB-PROBLEM NO.   6
    P=          .97656E-03
    ITERATION NUMBER  4
X(I)=
 .1226673        .1502621E-01  3.430039       1.234104       7.907810
 .2489033E-04    .1156306E-04  .4615884E-04   .2441183E-04   .2334688E-04
 .6794253E-04    .6541688E-04  .1081402E-03   .9311446E-04   .1734073E-04
 .9312689E-05    .6963774E-05  .1941709E-04   .1380753E-04   .1444773E-04




 11.25823
 M= -428.7217
 VALUE FOR F   -430.0912
 VALUE FOR THE EQUALITY CONSTRAINTS
  .42354643E-07   -.23589979E-03     .14539458E-01
```

```
 SUB-PROBLEM NO.   7
     R=          .24414E-03
    ITERATION NUMBER   4
X(I)=
 .1010762      .1520894E-01  3.425300      1.235223      7.907641
 .4324723E-05  .2046318E-05  .1272581E-04  .6317221E-05  .7353376E-05
 .2444773E-04  .1674987E-04  .2513225E-04  .2328265E-04  .4335557E-04
 .2324247E-05  .2743965E-05  .4854527E-05  .3452130E-05  .3612055E-05
11.26403
Ms -429.6739
VALUE FOR F   -429.7773
VALUE FOR THE EQUALITY CONSTRAINTS
 .2649769E-08   -.6932543EE-04      .3674912IE-02

 SUB-PROBLEM NO.   8
     R=          .931366E-04
    ITERATION NUMBER   4
X(I)=
 .1010826      .1502460E-01  3.424117      1.235254      7.907604
 .1107923E-05  .7466641E-06  .3216759E-05  .1636547E-05  .1921946E-05
 .6122179E-05  .4097444E-05  .6258198E-05  .5823915E-05  .1063913E-04
 .6P2C4A6E-06  .4352519E-06  .1213649E-05  .8630517E-06  .9130214E-06
11.26569
Ms -429.6732
VALUE FOR F   -429.6959
VALUE FOR THE EQUALITY CONSTRAINTS
 .1663579IE-09   -.1476J456E-04      .9387339E-03

 SUB-PROBLEM NO.   9
     R=          .152596E-04
    ITERATION NUMBER   3
X(I)=
 .1017562      .1497817E-01  3.423621      1.235312      7.907595
 .2817511E-06  .1974034E-06  .8414016E-06  .4231720E-06  .4984566E-06
 .1697502E-05  .1121835E-05  .1664542E-05  .1456246E-05  .2743767E-05
 .1486210E-04  .1088132E-04  .3.341298E-06  .2157637E-06  .2257550E-06
11.26586
Ms -429.6725
VALUE FOR F   -429.6792
VALUE FOR THE EQUALITY CONSTRAINTS
 .1C1455J2E-10   -.3690J236E-05      .2271829JE-03

 SUB-PROBLEM NO.  10
     R=          .321479E-05
    ITERATION NUMBER   3
X(I)=
 .1017494      .1496654E-01  3.423747      1.235326      7.907593
 .7277182E-07  .4842728E-07  .2226433E-06  .1109793JE-06  .1321699E-06
 .7292326E-06  .2956468E-06  .3911351E-06  .3638121E-06  .6774501E-06
 .3637926E-07  .2720331E-07  .7581325E-07  .5394398E-07  .5643099E-07
11.26595



Ms -429.6725
VALUE FOR F   -429.6743
VALUE FOR THE EQUALITY CONSTRAINTS
 .625277612-12   -.9225J393L-06      .5679574SE-04
```

back

```
 SUB-PROBLEM NO.  11
    R=          .6836?7E-06
    ITERATION NUMBER   3
X(I)=
 .1017455       .1496364E-01  3.423728       1.235330       7.907593
 .1667613E-07   .1232078E-07  .5949214E-07   .2554362E-07   .3407459E-07
 .9565817E-07   .6386620E-07  .9778375E-07   .3?963?0E-07   .1693626E-06
 .2?94?43E-08   .6600827E-06  .1896333E-07   .1348525E-07   .1410975E-07
 11.26599
 M= -429.6726
 VALUE FOR F   -429.6731
 VALUE FOR THE EQUALITY CONSTRAINTS
  .5584341?E-13    -.2306439?E-06     .141989?7E-04

 SUB-PROBLEM NO.  12
    R=          .23?42E-06
    ITERATION NUMBER   3
X(I)=
 .1017450       .1496291E-01  3.423724       1.235331       7.907593
 .4766334E-08   .3135603E-08  .1695156E-07   .7431284E-08   .8934?68E-08
 .2391465E-07   .1596655E-07  .2444594E-07   .2273?26E-07   .4234065E-07
 .2277?7?E-08   .1700207E-08  .4740632E-08   .3371313E-08   .3527437E-08
 11.26599
 M= -429.6726
 VALUE FOR F   -429.6728
 VALUE FOR THE EQUALITY CONSTRAINTS
  0.               -.57662419E-07     .35497342E-05

 SUB-PROBLEM NO.  13
    R=          .596056E-07
    ITERATION NUMBER   3
X(I)=
 .1017449       .1496273E-01  3.423723       1.235331       7.907593
 .1?2?667E-08   .?08?509E-08  .4297039E-08   .1937457E-08   .2347715E-08
 .6?9?6?5E-08   .3991637E-08  .6211494E-08   .5564570E-08   .1055516E-07
 .5548?54E-09   .4?50617E-09  .1189?J6E-08   .8428281E-09   .8318594E-09
 11.26599
 M= -429.6726
 VALUE FOR F   -429.6727
 VALUE FOR THE EQUALITY CONSTRAINTS
  0.               -.14415718E-07     .88743354E-06

 SUB-PROBLEM NO.  14
    R=          .1490?E-07
    ITERATION NUMBER   3
X(I)=
 .1017443       .1496268E-01  3.423722       1.235331       7.907593
 .3170364E-08   .2032837E-08  .1165814E-08   .5060441E-09   .6182443E-09
 .1404669E-08   .9979094E-09  .1527871E-08   .1421142E-08   .2646291E-08
 .1421065E-09   .1062629E-09  .2963020E-09   .2107?7JE-09   .2204648E-09
 11.26599
 M= -429.6727




 VALUE FOR F   -429.6727
 VALUE FOR THE EQUALITY CONSTRAINTS
  0.               -.36036728E-09     .22185844E-06


 **OBJECTIVE FUNCTION EVALUATED     94 TIMES
```

APPENDIX 5

USER'S GUIDE FOR OPTIMIZATION PROGRAM

This appendix presents a brief user's guide to the optimization programme. The variables read into the programme are defined and the sequence of cards read is given. The values denoted by an asterisk (*) are those used during this project.

OPTIMIZATION VARIABLES

CA — After each sub-problem, the value for R is divided by CA (suggested value CA = 4)

DIVE — Relative spread for the numerical estimate of the derivatives (suggested value DIVE = 10^{-6})

EPS1 — Convergence criterion for the objective function (suggested value EPS1 = 10^{-6})

EPS2 — Convergence criterion for correcting the objective function (suggested value EPS2 = 10^{-10})

EPSF — Convergence criterion for each sub-problem (suggested value EPSF = 10^{-5})

IDER — Method for calculating derivatives

- = 0* analytical first and second derivatives provided
- = 1 analytical first derivatives provided; second derivatives are calculated numerically
- = 2 both first and second derivatives are calculated numerically

IFIN — Calculations for each sub-problem are stopped for one of the following reasons:

- = 1* the gradient of the objective function no longer varies
- = 2 the value of the objective function no longer varies
- = 3 the norm of the correction vector no longer varies

IGAIN

- = 0 each descent step is not modified
- = 1* each descent step is modified to take into account the gain hoped for; IGAIN has no significance if IROPT = 0

IMET — Method used to construct the objective function

- = 0 exterior points
- = 1* mixed

IMPRIM — Print control variable

- = 0 print only the final optimization result
- = 1* print the result of each sub-problem
- = 2 print the result of each iteration

IPOS

- = 0 the variables of the objective function may be either positive or negative
- = 1* the variables of the objective function must be greater than zero

IPROB — Control variable

- = 1* computations are continued after the problem has been solved
- > 1 control is returned to the subroutine used to read thermodynamic data

IROPT — Modification to Newton's optimization

- = 0 optimum steps
- = 1* descent steps

IVER — Verification of analytical derivatives by comparing their value at the initial point with numerical estimates of the derivatives

- = 0 no verification
- = 1 verification of derivatives only
- = 2* verification of derivatives followed by solution of the optimization problem

K1 — The Hessian matrix is calculated each K1 iterations (suggested value K1 = 1)

KEX — Attempt to extrapolate to a more accurate solution

- = 0* no extrapolation
- = 1 extrapolation

LECT	= 1* the values for the following variables are given by the user and the rest are automatically given the suggested values by the program: N, NCI, NCE, X, IMET, IPOS, LECT, IMPRIM, IDER, IROPT, IGAIN, K1, IVER, KEX, IPROB
	= 2 values for the above are given by the user plus R, CA, NMAX, NPMAX
	= 3 all values mentioned above plus the following are given by the user: IFIN, TAU1, TAU2, EPS1, EPS2, EPSF, DIVE, XLIM
N	Number of variables in the objective function
NCE	Number of equality constraints
NCI	Number of inequality constraints
NPMAX	Maximum number of calculations of the objective function (suggested value NPMAX = 3000)
NMAX	Maximum number of sub-problems (suggested value NMAX = 20)
R	Penalty coefficient for the first sub-problem (suggested value R = 1)
TAU1	Convergence criterion for the gradient (suggested value TAU1 = 10^{-5})
TAU2	Second convergence criterion for the gradient (suggested value TAU2 = 10^{-5})
X	Vector in the main program, TT, containing the initial estimates of the variables in the objective function
XLIM	Precision required for the Powell method (suggested value XLIM = 10^{-6})

THERMODYNAMICS VARIABLES

A,B,C,D,	Vectors in subroutine ENTREE containing respectively the first, second, third and fourth constants of the heat capacity equation for the chemical components in the system
A1,B1,C1,D1	Vectors containing respectively the first, second, third and fourth constants of the heat capacity equation for the pure elements in the system
A	Two dimensional array in subroutine MODEL containing the first Redlich-Kwong coefficients of the chemical components
B	Vector in subroutine MODEL containing the second Redlich-Kwong coefficients of the chemical components
CM	Two dimensional array containing the number of atoms of each element in the chemical components
DIV	Vector containing the number of atoms in each pure element
DNOM	Character vector containing the names of the chemical components
EL	Character vector containing the names of the elements in the system
GREF	Vector containing the free energy of formation of the chemical components at a standard reference temperature
HREF	Vector containing the enthalpy of formation of the chemical components at a standard reference temperature
IFPRNT	Print control variable = 0 print only the final answer > 0* print input thermodynamic data, change of state calculations and the final answer
PP	Reaction pressure (in atmospheres)
REF	Reference temperature (usually, REF = 298.15 K)
T	Reaction temperature (in K)

X — Vector in ENTREE containing the total number of each element in the system

Y — Vector containing a gas phase parameter for the chemical components

= 0 not a gas

= 1 gas

Z — Vector containing a liquid phase parameter for the chemical components

= 0 not a liquid

= 1 liquid or gas dissolved in liquid

INPUT CARDS

All variables are read in free format.

Case 1: when LECT = 1

sources	card numbers	variables
TT	1	N, NCI, NCE
TT	2	X(I), I = 1, N
TT	3	IMET, IPOS, LECT, IMPRIM, IDER
TT	4	IROPT, IGAIN, K1, IVER, KEX, IPROB
ENTREE	5	IFPRNT
ENTREE	6	EL(I), A1(I), B1(I), C1(I), D1(I), DIV(I), X(I)
	:	:
	to 5+N	I = 1, N
	:	:
ENTREE	6+N	T, PP, REF
ENTREE	7+N	DNOM(I), Y(I), Z(I)
ENTREE	8+N	CM(I,J), J = 1, NCE
ENTREE	9+N	A(I), B(I), C(I), D(I), HREF(I), GREF(I)
	:	:
	to 6+N+3N	I = 1, N
	:	:

Sources	Card Numbers	Variables
MODEL	7+4N	A(I,I), B(I)
	:	:
	to 7+4N+N	I = 1, N
	:	:
	end	

Case 2: when LECT = 2

sources	card numbers	variables
TT	1-4	as in case 1
TT	4a	R, CA, NMAX, NPMAX
ENTREE, MODEL	5-end	as in case 1

Case 3: when LECT = 3

sources	card numbers	variables
TT	1-4a	as in case 2
TT	4b	IFIN, TAU1, TAU2, EPS1, EPS2, EPSF, DIVE, XLIM
ENTREE, MODEL	5-end	as in case 1